

STUDIES ON THE MECHANISMS OF
COPOLYMERIZATION OF ELECTRON-DONOR DIENES
AND ELECTRON-ACCEPTOR DIENES

BY

JEN-CHI CHEN

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1985

To my family, for their love,
patience and encouragement

ACKNOWLEDGMENTS

I would like to express my deep appreciation and gratitude to my research director, Professor George B. Butler, for his encouragement and guidance during the course of this work. I would also like to acknowledge the members of my supervisory committee for their valuable time.

The friendship and cooperation provided by my colleagues in the polymer chemistry laboratories are greatly appreciated.

I would like to thank Miss Cindy Zimmerman for her skillful typing of this manuscript. I also wish to thank my wife, Weng-Jang, for her encouragement and patience.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS.....	iii
LIST OF TABLES.....	vi
LIST OF FIGURES.....	viii
ABSTRACT.....	xi
 CHAPTERS	
I INTRODUCTION.....	1
General Background.....	1
Mulliken's Valence Bond Treatment.....	1
Molecular Orbital Treatment.....	4
Basic Principles of Copolymerization.....	6
Diels-Alder Reaction.....	12
Copolymerization of Conjugated Diene and Dienophile.....	13
The Research Objectives.....	17
II EXPERIMENTAL.....	18
General Information.....	18
Reagents and Solvents.....	19
Monomer Synthesis.....	19
Copolymer Synthesis.....	34
Copolymerizations in Aqueous Phase.....	45
Monomer Reactivity Ratios.....	46
Copolymer Characterization.....	48
Complexation Studies.....	54
Diels-Alder Reactions with Inverse Electron Demand.....	58
III RESULTS AND DISCUSSION.....	60
Polymerizations of Electron-Poor Dienes with	
Electron-Rich Dienophiles.....	60
Copolymerizations of Electron-Rich Dienes with	
Electron-Poor Dienophiles.....	75

Copolymerizations of Electron-Rich Dienes with	
Electron-Poor Dienes.....	111
Copolymerizations in Aqueous Phase.....	118
Summary and Conclusions.....	121
REFERENCES.....	123
BIOGRAPHICAL SKETCH.....	126

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Conditions for the Polymerizations of Methyl 2,4-Pentadienoate (MPD) with Electron-Rich Dienophiles.....	35
2 Yields and Analysis Data for Polymers in Table 1.....	36
3 Conditions for the Polymerizations of 1-Carboethoxy- 1-cyano-1,3-butadiene (CCB) with Electron-Rich Dienophiles.....	37
4 Yields and Analysis Data for Polymers in Table 3.....	38
5 Conditions for the Copolymerizations of Acrylonitrile (AN) with Electron-Rich Dienes.....	39
6 Yields and Analysis Data for Copolymers in Table 5.....	40
7 Conditions for the Copolymerizations of Electron-Rich Dienes (ERD) with Electron-Poor Dienes (EPD).....	41
8 Yields and Analysis Data for Copolymers in Table 7.....	42
9 Conditions for the Polymerizations of Some Electron- Rich Monomers (ERM) with Some Electron-Poor Monomers (EPM).....	43
10 Yields and Analysis Data for Polymers in Table 9.....	44
11 Conditions and Results of Polymerizations of Water Soluble Monomers.....	45
12 Conditions, Yields and Analysis Data for the Copolymerizations of Acrylonitrile (AN) with 1-Ethoxy-1,3-butadiene (EBD).....	46
13 Conditions, Yields and Analysis Data for the Copolymerizations of Acrylonitrile (AN) with 1-Diethylamino-1,3-butadiene (DABD).....	47
14 ¹ H NMR Data for Determination of Formation Constant of Complexation of AN-EBD System at 25°C.....	55

15	^1H NMR Data for Determination of Formation Constant of Complexation of AN-EBD System at 60°C.....	56
16	^1H NMR Data for Determination of Formation Constant of Complexation of AN-DABD System at 25°C.....	57
17	^{13}C NMR Data for the Complexed and Uncomplexed EBD Molecules.....	57
18	^{13}C NMR Data for the Complexed and Uncomplexed DABD Molecules.....	58
19	Conditions and Results for Diels-Alder Reactions with Inverse Electron Demand.....	59
20	Monomer Reactivity Ratios and Alfrey-Price Q and e Values for the Free Radical Initiated Copolymerization of EBD and AN.....	82
21	Assignments of Chemical Shifts in ^1H NMR Spectrum of AN-EBD Copolymer.....	84
22	Assignments of Chemical Shifts in ^{13}C NMR Spectrum of AN-EBD Copolymer.....	86
23	Monomer Reactivity Ratios for the Free Radical Initiated Copolymerization of DABD and AN.....	97
24	Assignments of Chemical Shifts in ^1H NMR Spectrum of AN-DABD Copolymer.....	100
25	Assignments of Chemical Shifts in ^{13}C NMR Spectrum of AN-DABD Copolymer.....	100
26	Assignments of Chemical Shifts in ^1H NMR Spectrum of AN-TSBD Copolymer.....	105
27	Assignments of Chemical Shifts in ^{13}C NMR Spectrum of AN-TSBD Copolymer.....	106
28	Assignments of Chemical Shifts in ^{13}C NMR Spectrum of AN-ATBD Copolymer.....	110

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 The Energy-Level Diagram of the Weak Charge-Transfer Complex.....	3
2 Molecular Orbital Representation of a Weak Charge-Transfer Complex.....	4
3 The Possible Reaction Pathways Form Alternating Copolymers.....	9
4 The Reaction Pathways of Diels-Alder Reaction.....	12
5 Frontier Orbital Interactions in the Diels-Alder Reactions.....	14
6 ^1H NMR (60 MHz) Spectrum of Methyl 2,4-Pentadienoate in CDCl_3 at 25°C	63
7 ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of Methyl 2,4-Pentadienoate in CDCl_3 at 25°C	64
8 ^1H NMR (60 MHz) Spectrum of Poly(Methyl 2,4-Pentadienoate) in CDCl_3 at 25°C	65
9 ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of Poly(Methyl 2,4-Pentadienoate) in CDCl_3 at 25°C	66
10 ^1H NMR (60 MHz) Spectrum of Poly(1-Carbethoxy-1-cyano-1,3-butadiene) in CDCl_3 at 25°C	70
11 ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of Poly(1-Carbethoxy-1-cyano-1,3-butadiene) in CDCl_3 at 25°C	71
12 Frontier Orbital Energies and Coefficients for 1-Substituted Dienophile Donors and 1-Substituted Diene Acceptors.....	73
13 Monomer Feed-Copolymer Composition Curve for Copolymerization System of EBD and AN.....	76

14	^1H NMR Spectra of AN-EBD Copolymers, Except D (Spontaneous Initiation), the Others Prepared with Free Radical Catalysts. Copolymer Compositions of EBD(%): (A) 14.9; (B) 49.6; (C) 50.6; (D) 52.3; (E) 54.0; (F) 57.5.....	77
15	^1H Decoupled ^{13}C NMR Spectra of AN-EBD Copolymers, Except D (Spontaneous Initiation), the Others Prepared with Free Radical Catalysts. Copolymer Compositions of EBD(%): (A) 14.9; (B) 49.6; (C) 50.6; (D) 52.3; (E) 54.0; (F) 57.5.....	78
16	Plot According to the Method of Fineman-Ross for the AN-EBD Copolymer System.....	80
17	Plot According to the Method of Kelen-Tudos for the AN-EBD Copolymer System.....	81
18	^1H NMR (60 MHz) Spectrum of AN-EBD Copolymer in CDCl_3 at 25°C	83
19	^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of AN-EBD Copolymer in CDCl_3 at 25°C	85
20	Frontier Orbital Energies and Coefficients for 1-Substituted Dienophile Acceptors and 1-Substituted Diene Donors.....	93
21	Plot According to the Method of Fineman-Ross for the AN-DABD Copolymer System.....	95
22	Plot According to the Method of Kelen-Tudos for the AN-DABD Copolymer System.....	96
23	^1H NMR (60 MHz) Spectrum of AN-DABD Copolymer in CDCl_3 at 25°C	98
24	^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of AN-DABD Copolymer in CDCl_3 at 25°C	99
25	^1H NMR (60 MHz) Spectrum of AN-TSBD Copolymer in CDCl_3 at 25°C	103
26	^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of AN-TSBD Copolymer in CDCl_3 at 25°C	104
27	^1H NMR (60 MHz) Spectrum of AN-ATBD Copolymer in CDCl_3 at 25°C	108

28	^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of AN-ATBD Copolymer in CDCl_3 at 25°C	109
29	^1H NMR (60 MHz) Spectrum of MPD-EBD Copolymer in CDCl_3 at 25°C	112
30	^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of MPD-EBD Copolymer in CDCl_3 at 25°C	113
31	^1H NMR (60 MHz) Spectrum of MPD-ATBD Copolymer in CDCl_3 at 25°C	116
32	^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of MPD-ATBD Copolymer in CDCl_3 at 25°C	117
33	^1H NMR (60 MHz) Spectrum of Poly(Trimethyl Vinyl Ammonium Acrylate) in D_2O at 25°C	119
34	^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of Poly(Trimethyl Vinyl Ammonium Acrylate) in D_2O at 25°C	120

Abstract of Dissertation Presented to the Graduate School
of the University of the Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

STUDIES ON THE MECHANISMS OF
COPOLYMERIZATION OF ELECTRON-DONOR DIENES
AND ELECTRON-ACCEPTOR DIENES

BY

JEN-CHI CHEN

August, 1985

Chairman: Dr. George B. Butler
Major Department: Chemistry

The aim of this research was to study the mechanism of
alternating copolymerizations of diene-dienophile systems.

The copolymerizations of electron-poor dienes with electron-rich
dienophiles, electron-rich dienes with electron-poor dienophiles, and
electron-rich dienes with electron-poor dienes were investigated.

The microstructure and sequence distributions of monomers in the
resulting polymers were analyzed by IR, ^1H NMR and ^{13}C NMR
techniques.

In the polymerization system of diene acceptors (methyl 2,4-
pentadienoate; 1-cyano-1,3-butadiene; and 1-carbethoxy-1-cyano-1,3-
butadiene) with several vinyl ethers, the resulting polymers were
found to be composed of diene monomer units only.

In the copolymerization system of diene donors (1-ethoxy-1,3-butadiene; 1-diethylamino-1,3-butadiene; 1-trimethylsilyloxy-1,3-butadiene; and 1-acetoxy-1,3-butadiene) with acrylonitrile, the resulting copolymers were found to have a high alternating structure.

In the copolymerizations of acrylonitrile with 1-ethoxy-1,3-butadiene and 1-diethylamino-1,3-butadiene, the monomer reactivity ratios were determined by the Fineman-Ross and Kelen-Tudos methods.

On the basis of chemical shift differences between the head-to-tail and head-to-head monomer sequence distributions, the mechanism of this alternating copolymerization system was suggested.

In the copolymerization system of several diene donors with several diene acceptors, it was found that the mole fractions of acceptors were much more than those of donors in the resulting copolymers.

In order to explain all these copolymerization systems, a frontier molecular orbital treatment was proposed. A good qualitative correlation with experimental results was obtained.

CHAPTER I INTRODUCTION

General Background

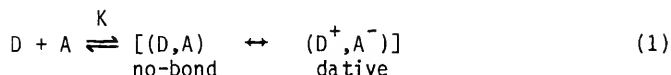
When electron donors and electron acceptors are brought together, they usually form electron donor-acceptor complexes to various extents. The term "electron donor-acceptor complex" is used to describe a wide variety of intermolecular complexes. Its range comprises Lewis acid-Lewis base interactions, ion pairs, and charge-transfer complexes. The enthalpies of dissociation of these complexes are much smaller than those of ordinary chemical reactions, and are similar to hydrogen bondings and van der Waals forces.

In 1949, Benesi and Hildebrand¹ measured the ultraviolet spectra of iodine and benzene in n-heptane solutions and discovered a new absorption band which is uncharacteristic of either of the component molecules. Later, Mulliken^{2,3} successfully developed a now widely accepted theoretical description of these phenomena. Mulliken's contribution has stimulated a wide variety of theoretical and experimental work in this area.

Mulliken's Valence Bond Treatment

On the basis of the valence bond theory, Mulliken described the complex that exists in a resonance form between the no-bond and the

dativ states of the donor molecule (D) and the acceptor molecule (A).



where (D,A) is the no-bond state of the complex, (D⁺,A⁻) is the dative state of the complex, and K is the formation constant of the complex.

The wave functions of the complex can be expressed as a linear combination of wave functions of the no-bond state and the dative state. The ground state:

$$\psi_N = a\psi_0(D,A) + b\psi_1(D^+,A^-) \quad (2)$$

with $a \gg b$

and the excited state:

$$\psi_E = b^*\psi_1(D^+,A^-) - a^*\psi_0(D,A) \quad (3)$$

with $b^* \gg a^*$

where $\psi_0(D,A)$ is the wave function for the molecular complex which is held together by several physical electrostatic forces involving dipole-dipole, dipole-induced dipole, London dispersion, and hydrogen bonding types. The term $\psi_1(D^+,A^-)$ correlates with a wave function for the complex where one electron has been entirely transferred from the donor molecule to the acceptor molecule. The transition between

these two states yields the characteristic charge-transfer absorption band. The term "charge-transfer complex" is usually given to this association pair.

For these weak charge-transfer complexes, their energy levels can be treated by the perturbation theory. The energy-level diagram of the relationship between the various terms is shown in Figure 1.

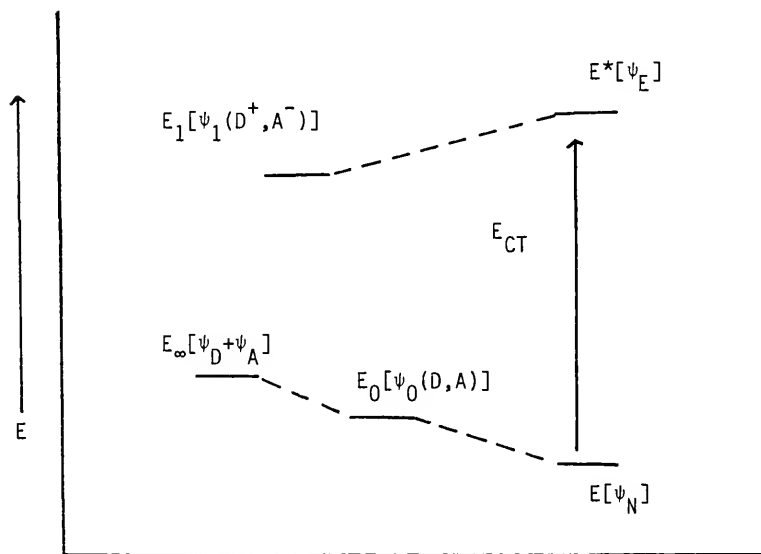


Fig. 1. The Energy-Level Diagram of the Weak Charge-Transfer Complex.

Based on Mulliken's treatment, a relationship among the energy of the charge-transfer transition (E_{CT}), the ionization potential of the donor (I_D), and the electron affinity of the acceptor (E_A) can be expressed by equation (4).

$$E_{CT} = I_D - E_A + G + X \quad (4)$$

where G and X are coulomb and resonance energies, respectively, and are considered to be constant for a given donor and acceptor. This expression has been well proven experimentally.

Molecular Orbital Treatment

About the same year, an alternative approach to this intermolecular charge-transfer transition was proposed by Dewar⁴ and Fukui,⁵ respectively. In their approaches, the complex is treated as a π -complex which is formed by the interaction of the π -orbitals of the donor and the acceptor. Since the interaction between donor and acceptor is very small, the charge-transfer interaction can also be treated by the perturbation method. The energy-level diagram of the molecular orbital representation of a weak charge-transfer complex is shown in Figure 2.

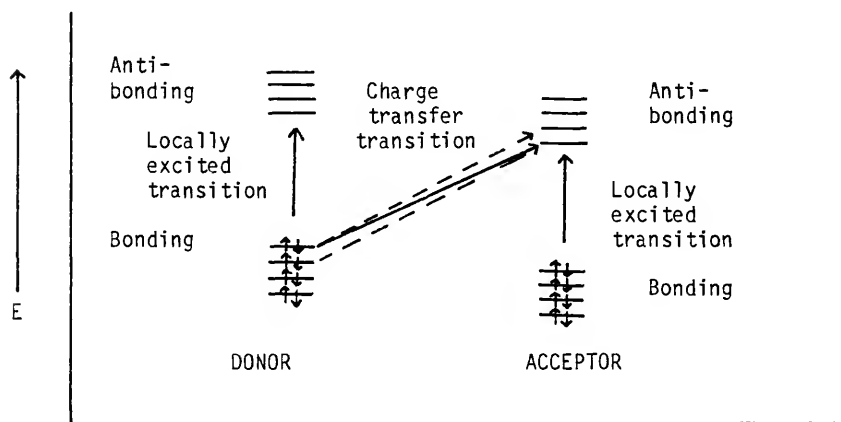


Fig. 2. Molecular Orbital Representation of a Weak Charge-Transfer Complex.

Interactions between occupied bonding orbitals of donors and acceptors produce no change in their total energy and no net transfer of charge between donor and acceptor. Interactions of the occupied orbitals of the donor with the unoccupied antibonding orbitals of the acceptor lower the former and elevate the latter, leading to a net stabilization with a transfer of negative charge from donor to acceptor. Interactions of the occupied orbitals of the acceptor with the unoccupied antibonding orbitals of the donor similarly produce stabilization with a net charge transfer in the opposite direction. These interactions are inversely proportional to the energy gap between the interacting orbitals. The donor is usually recognized as having the highest energy occupied molecular orbital (HOMO) and the acceptor is recognized as having the lowest energy unoccupied molecular orbital (LUMO). The interaction between LUMO and HOMO has been regarded as an important role in many organic reactions.

The molecular orbital approach arrives at a similar conclusion to that of the valence bond treatment, but it looks preferable for two reasons: first, some complexes show more than one new charge-transfer absorption band. This can be rationalized by the molecular orbital theory, because there should be a band correlating to the transition between any of the occupied orbitals of donor and any of the unoccupied orbitals of the acceptor; secondly, the term "charge-transfer complex" is misleading in that very little charge is transferred in the ground states of such complexes, but an appreciable part of their stability may be due to the back donation involving interactions between the occupied orbitals of the acceptor

and the unoccupied orbitals of the donor. It is obvious from both approaches that the charge-transfer forces will influence the structure of molecular complexes: the maximum amount of charge-transfer stabilization of the complex is to be expected when the overlap between these orbitals is greatest. The structure of π -conjugated donors and acceptors pile parallelly with the planes of the molecules, but offset slightly to each other.

The fact that charge-transfer absorption bands are observed does not mean that complexes play any significant role in the reaction. Conversely, failure to find charge-transfer absorption bands does not prove that a charge-transfer process is not involved, because in some cases, the transition energy for the charge-transfer absorption may be much greater than that required for the thermal charge-transfer process; the charge-transfer bands may overlap with the absorptions of the donor and/or the acceptor; the extinction coefficients of charge-transfer transitions may be much smaller than those of molecular electronic absorptions.

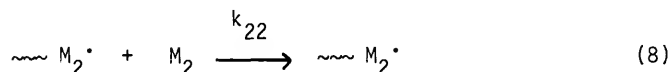
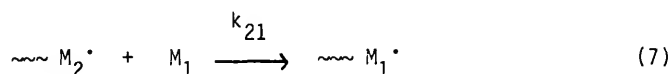
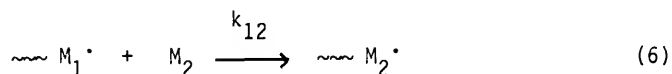
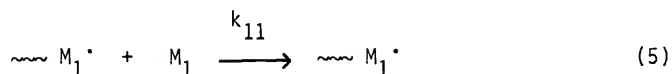
Kosower⁶ has reviewed those organic reactions in which charge-transfer complexes are frequently postulated as intermediates. The types of reactions discussed involve solvolysis, thermal electron transfer reactions, and reactions which follow light absorption by a charge-transfer complex.

Basic Principles of Copolymerization

In 1944 Mayo and Lewis⁷ successfully developed the first mathematical analysis of a polymerization system involving a mixture of two monomers. They considered the four propagation steps outlined

below, and then derived the copolymerization equation as shown below.

Four propagation steps:



Copolymerization equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] r_1 [M_1] + [M_2]}{[M_2] r_2 [M_2] + [M_1]} \quad (9)$$

Two equations of the propagation reactions are homopolymerizations or self-propagating steps, and the other two equations are heteropolymerizations or cross-propagating steps. M_1^\cdot and M_2^\cdot are used as symbols for the polymer chain end radicals with M_1 and M_2 terminal groups, respectively. The copolymerization equation allowed the copolymerization composition and sequence distribution to be related to the monomer feed composition through two monomer reactivity ratios, where $r_1 = k_{11}/k_{12}$, and $r_2 = k_{22}/k_{21}$. This equation has been proven to be very successful in explaining the experimental results for many copolymer systems, but there were several systems which

could not be satisfactorily explained. This equation was derived using several assumptions, i.e., bimolecular propagation mechanism, absence of the penultimate chain effect and depolymerization, high degree of polymerization, and identity of overall and effective concentrations.

Penultimate Chain End Effects

In order to explain some of these deviations, Alfrey and coworkers⁸ proposed that the reactivity of a chain end radical towards a particular monomer molecule could be influenced by the penultimate group in the growing chain. The mathematical treatment of this effect in this copolymerization system involves eight propagating steps and four reactivity ratios. This penultimate model was able to explain the results of several of those systems which deviate from the simple copolymerization equation (terminal model). An example is the styrene-fumaronitrile system.

Charge-transfer Complexes

An alternative approach to explaining deviations from the simple copolymerization equation was proposed by Bartlett and Nozaki,⁹ in 1946. They observed that the solution of styrene and maleic anhydride showed a yellow coloration. This coloration was attributed to the formation of an electron donor-acceptor complex between this monomer pair. Therefore, they proposed that the electron donor-acceptor complex may participate as a monomer in the propagation step of the polymerization. The mathematical treatment of this complex model involves eight propagation steps and six reactivity ratios.¹⁰

The role of the charge-transfer complex in the polymerization reaction has usually been classified into two categories: one is so-called "charge-transfer polymerization," the first proposes that the interaction between the donor and the acceptor may generate reactive species to initiate one or the other of the homopolymerization reactions; the other one proposes that alternating copolymerization will occur.

Alternating Copolymerization

Alternating copolymerizations are characterized by the fact that a nearly 1:1 molar ratio of the comonomers is found in copolymers produced from a wide variety of comonomer mole fractions in the initial monomer solution. The possible reaction pathways are shown in Figure 3.¹¹

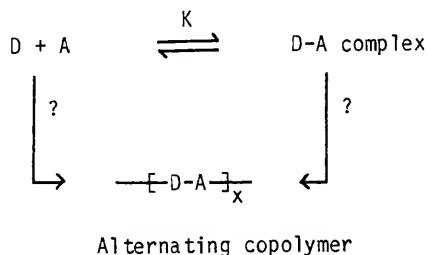


Fig. 3. The Possible Reaction Pathways Form Alternating Copolymers.

On the basis of these possible reaction pathways, three mechanisms have been proposed to explain this strong alternation tendency between the electron donor and the electron acceptor.

In 1946 Bartlett and Nozaki⁹ proposed the first mechanism in which the copolymerization is via a stable monomer complex composed of the two monomer units. This mechanism has been supported by the works of Butler and coworkers¹²⁻¹⁵ (maleic anhydride-divinyl ether and maleic anhydride-furan copolymers), Caze and Loucheux¹⁶ (maleic anhydride-vinyl acetate copolymer), Goethals and coworkers¹⁷ (maleic anhydride-benzofuran, maleic anhydride-indole, maleic anhydride-benzothiophene copolymers), Yamashita and coworkers^{18,19} (maleic anhydride-p-dioxene, maleic anhydride-1,2-dimethoxyethylene copolymers), and Gaylord and coworkers^{20,21} (maleic anhydride-conjugated diene copolymers). This mechanism is also called the "complex" mechanism.

Walling²² proposed the second mechanism in which electrostatic interactions between differently polarized monomers and radicals decrease the activation energy for the alternating chain propagation. This mechanism is also called the "free monomer" mechanism. Price and Alfrey²³ have rationalized these reactivities in terms of resonance and polar effects in a semi-empirical scheme known as the Q-e scheme. They proposed that the rate constant for a radical-monomer reaction, for example, for the reaction of M_1^\cdot radical with M_2 monomer, can be written as

$$k_{12} = P_1 Q_2 \exp (-e_1 e_2) \quad (10)$$

where P_1 and Q_2 are measures of the resonance stabilization of M_1^\cdot radical and M_2 monomer, respectively, and e_1 and e_2 are measures of

their polar properties. The e value is positive for electron-poor olefins and negative for electron-rich olefins. The monomer reactivity ratios may be expressed by the following equations:

$$r_1 = \frac{Q_1}{Q_2} \exp [-e_1(e_1 - e_2)] \quad (11)$$

$$r_2 = \frac{Q_2}{Q_1} \exp [-e_2(e_2 - e_1)] \quad (12)$$

The copolymerization tendency, $r_1 r_2$, is expressed in terms of e -values:

$$r_1 r_2 = \exp [-(e_1 - e_2)^2] \quad (13)$$

From this equation, the combination of two monomers having different e -values, especially those differing in sign, favors alternating copolymerization. However, another term, Q , is also important, and two monomers having very different Q -values fail to produce alternating copolymers, because of their different reactivities.

The third mechanism was proposed by Shirota²⁴ and Tsuchida,²⁵ respectively. This mechanism involves the participation of both free monomers and the charge-transfer complex monomer in the propagation steps. The idea of this mechanism originates from the fact that the initial copolymerization rate does not necessarily maximize at the monomer feed ratio of 1:1 where the concentration of the charge-transfer complex attains maximum, which is inconsistent with the second mechanism.

Diels-Alder Reaction

The Diels-Alder reaction was discovered about sixty years ago, because six-membered rings are formed with remarkable stereoselectivity and regioselectivity, this reaction is of great synthetic utility. Its mechanism has been suggested as either a concerted reaction or a stepwise reaction. In many cases, it has been regarded as a reversible reaction. The proposed reaction pathways for this reaction are shown in Figure 4.²⁶

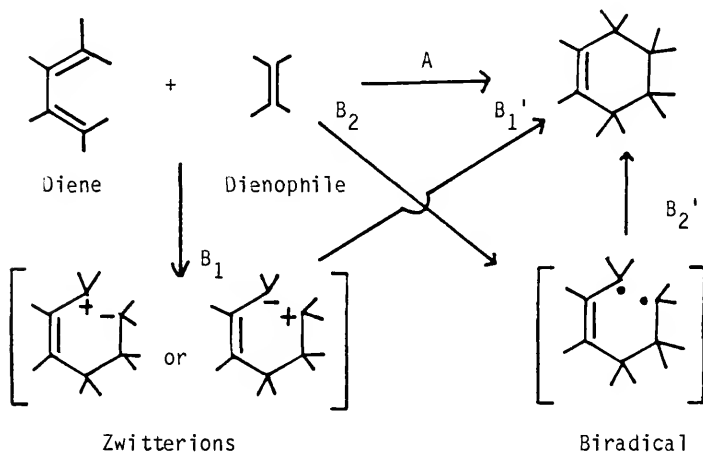


Fig. 4. The Reaction Pathways of Diels-Alder Reaction.

The new σ bonds between the reactants may be formed simultaneously in a multicenter mechanism, as shown in reaction pathway A, involving a one step reaction whose energy profile contains only one activation barrier. Another possibility is that the two bonds are formed in two successive reaction steps. The energy profile of this two step

reaction contains two transition states and one intermediate, i.e., either a zwitterion or a biradical.

Although the reaction occurs in the unsubstituted diene-dienophile system, it is most successful when the diene and dienophile contain substituents of supplementary electronic influence. Alder found that the reaction rate is often increased by electron-donating substituents on the diene and by electron-accepting substituents on the dienophile. This phenomenon has been rationalized by frontier orbital theory treatment, and is the so-called "Diels-Alder reaction with normal electron demand." There are some examples that illustrate inverse electron demand, i.e., electron-accepting substituents on the diene and electron-donating substituents on the dienophile. However, they are unable to find a suitable model system. The frontier orbital interactions of all these diene-dienophile systems, i.e., unsubstituted, normal electron demand, and inverse electron demand, are shown in Figure 5.²⁷ On the basis of the energy gap of the HOMO-LUMO interactions, the reaction rates of both "normal electron demand" and "inverse electron demand" diene-dienophile systems should be faster than those of unsubstituted diene-dienophile systems.

Copolymerization of Conjugated Diene and Dienophile

In 1970 Butler and coworkers¹³ studied the copolymerization of furan and maleic anhydride, and found that a 1:1 copolymer of these comonomers was produced, regardless of the monomer feed ratios. The

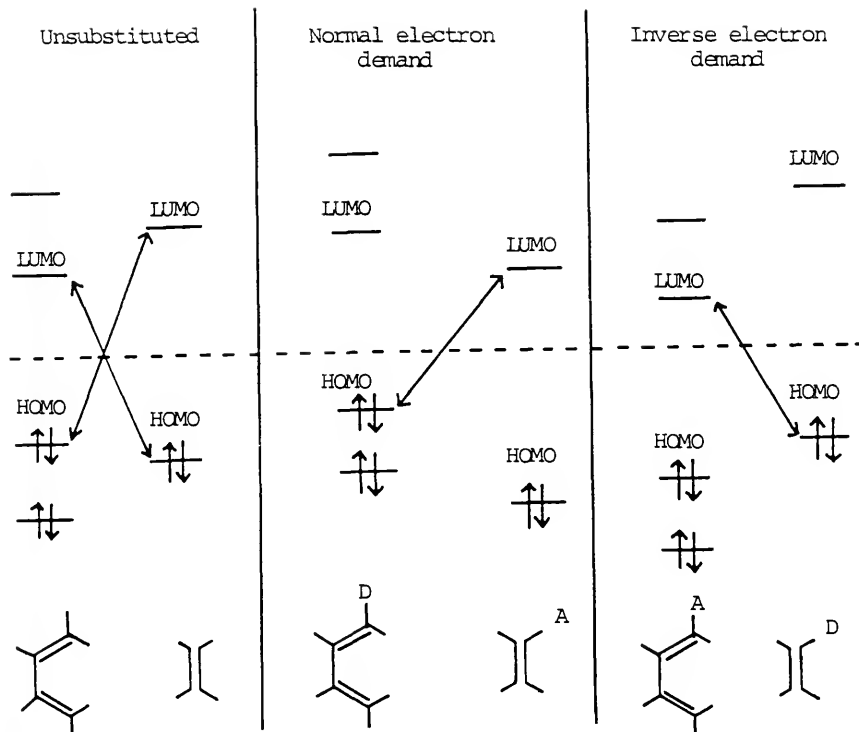
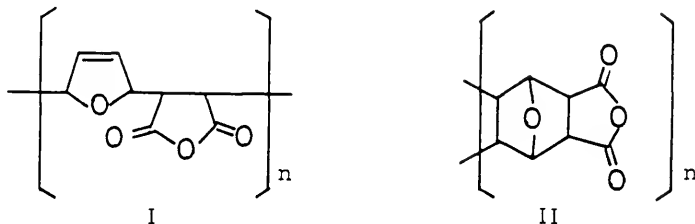


Fig. 5. Frontier Orbital Interactions in the Diels-Alder Reactions.²⁷

presence of a donor-acceptor complex between the monomers was observed by NMR and UV methods. Therefore, they proposed that the polymerizations proceeded by homopolymerization of this complex to produce an alternating sequence in the copolymer.

In 1976¹⁴ and 1981¹⁵ Butler and Ragab reported further studies on the mechanism of this copolymerization, and showed the copolymer was comprised of alternating monomer units as in structure I instead

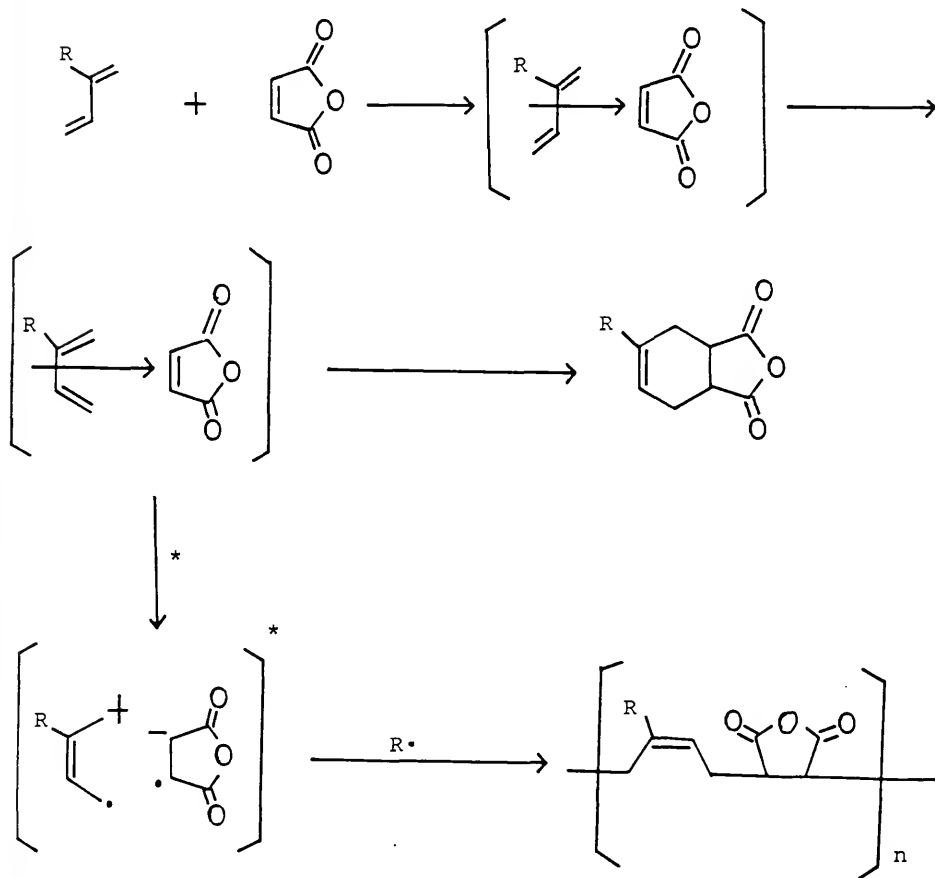
of structure II, i.e., the homopolymer of the exo form of the Diels-Alder adduct.



They also studied copolymerization of a number of furan derivatives with maleic anhydride, comparing the copolymer microstructures with those of model compounds. They made a comparative study of various donors and acceptors related to furan and maleic anhydride and concluded that the trend among the initial polymerization rates was analogous to that among the equilibrium constants for complex formation. On the basis of their studies they suggested that the donor-acceptor complex is the active polymerizing species.

Gaylord and coworkers have made wide-ranging studies of the free radical copolymerization of maleic anhydride with conjugated dienes, i.e., butadiene,²⁰ pentadienes,²¹ and cyclopentadienes.²⁸ They postulated that the cyclic adduct and the alternating copolymer arise from a common intermediate, i.e., the charge-transfer complex as a result of intramolecular and intermolecular reactions, respectively. The cyclic adduct was proposed to be formed from the complex in the ground state, and the alternating copolymer from the complex

in the excited state. The general mechanism for reactions of linear dienes and maleic anhydride proposed by Gaylord and coworkers is shown below:



The Research Objectives

In order to gain further insight into the mechanism of the alternating copolymerizations of diene-dienophile systems and the relationship between the copolymerization and the Diels-Alder reactions, the copolymerizations of electron-poor dienes with electron-rich dienophiles, electron-rich dienes with electron-poor dienophiles, and electron-rich dienes with electron-poor dienes were investigated.

The microstructures and sequence distributions of monomers in the resulting polymers were analyzed by IR, ^1H NMR, and recent developments of ^{13}C NMR techniques.

On the basis of the chemical shift differences between the head-to-tail and head-to-head monomer sequence distributions, the mechanisms of these copolymerization systems were suggested.

CHAPTER II EXPERIMENTAL

General Information

All temperatures are uncorrected and are reported in degrees centigrade. Melting points were determined in open capillary tubes using a Thomas-Hoover melting point apparatus. Pressures are expressed as millimeters of mercury. Elemental analyses were performed by either Atlantic Microlab. Inc., Atlanta, Georgia, or the University of Florida, Department of Chemistry, Gainesville, Florida. Infrared spectra were recorded on a Perkin-Elmer Model 281 Infrared Spectrophotometer. Spectra were calibrated by using the 1601 cm^{-1} line of a polystyrene film. Spectra of liquids were performed neat as a smear on potassium chloride plates, and those of solids were obtained by using KBr pellets. Vibrational transition frequencies are expressed in wavenumber (cm^{-1}) with the intensity of the bands being assigned the following classifications: weak (w), medium (m), strong (s), very strong (vs), and broad (br). Proton nuclear magnetic resonance (NMR) spectra (60 MHz) were recorded on a Varian EM-360L Spectrometer. Carbon-13 (25.2 MHz) and proton (100 MHz) NMR spectra were obtained on a Jeol JNM-FX-100 instrument. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) unless stated otherwise. Multiplicities

of proton and off-resonance decoupled ^{13}C resonances are designated as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). Coupling constants (J) are expressed in Hertz (Hz). Ultra-violet and visible spectra were measured with a Perkin-Elmer 330 Spectrophotometer. Intrinsic viscosities were measured by standard procedures using a Cannon-Ubbelohde Semimicro Viscometer (dilution viscometer).

Reagents and Solvents

Reagents were obtained from Fisher Scientific Co., or Aldrich Chemical Co., unless otherwise noted. Deuterated NMR solvents were obtained from Merck & Co., Inc., and Aldrich Chemical Co., and were used without further purification.

All solvents used for general application were of reagent grade or ACS grade quality. For special purposes, purification of solvents was carried out by the following procedures reported in the handbook.²⁹

Monomer Synthesis

Ketene, Diethylacetal(1)³⁰

The reaction was conducted in a 500 ml round-bottomed flask attached to a reflux condenser, the top of which was connected to a three-way stopcock leading to a source of nitrogen gas and a mercury trap, and a water aspirator. The flask and condenser were dried by warming with a free flame while the system was under reduced pressure, then dry nitrogen was admitted to the apparatus. The cooled flask was quickly charged with 205 ml of dry tert-butyl

alcohol and 9.15 g (0.234 mole) of potassium and was then reconnected to the apparatus. The flow of nitrogen was stopped and the mixture was boiled under reflux until the potassium was entirely reacted, hydrogen being liberated through the mercury trap. The solution was then cooled slightly while nitrogen was admitted to equalize the pressure. The flask was quickly disconnected just long enough for the addition of 35.60 g (0.233 mole) of chloroacetaldehyde diethylacetal. A white precipitate of potassium chloride began to deposit immediately. The flask was attached at once to a Vigreux column wrapped with a heating tape, the top of column was connected to a total-reflux partial take-off still head. The tert-butyl alcohol was distilled at the ratio of 25 drops per minutes with a reflux ratio at the still head of about 6:1. This operation required about 5-6 hours. At the end of this time, the temperature of the oil bath was raised to 160° and maintained there until no more alcohol came over. The bath was then allowed to cool while the pressure of the fractionating system was gradually reduced to 200 mm Hg. The product was collected; yield: 13.4 g (49.4%); b.p. 83-86° at 200 mm Hg (lit. rep. 67-75%).

^1H NMR (60 MHz, CDCl_3): δ 1.32 (t, 6H, $J = 7.2$ Hz), 3.10 (s, 2H), 3.84 (q, 4H, $J=7.2$ Hz).

^{13}C NMR (CDCl_3): δ 14.37, 55.46, 63.42, 164.97.

IR (neat): 3148 (w), 2980 (m), 2938 (m), 2890 (s), 1740 (m), 1648 (s), 1480 (m), 1445 (m), 1388 (m), 1372 (m), 1282 (s), 1190 (m), 1162 (m), 1084 (m), 1050 (s), 972 (m), 948 (m), 874 (m), 804 (w), 710 (m) cm^{-1} .

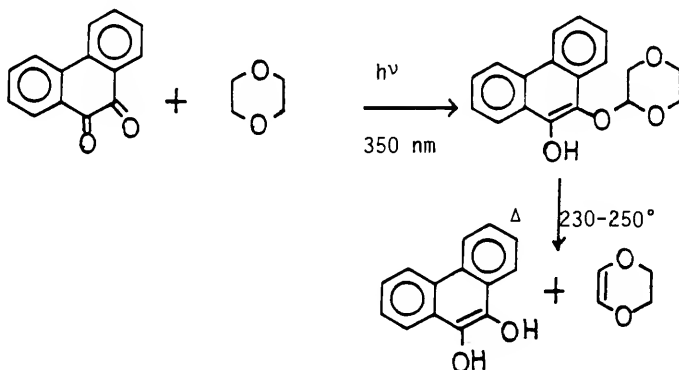
Ketene, Dimethylacetal (2)³¹

In a 500 ml three-necked round-bottomed flask equipped with a thermometer, a mechanical stirrer, and a Vigreux column, which was fitted with a total-reflux partial take-off still head, were charged 220 ml of anhydrous pinacol and 10.6 g (0.461 mole) of sodium. The mixture was heated and stirred until all the sodium had reacted. The solution was cooled to 160° with stirring and 47.5 g (0.381 mole) of chloroacetaldehyde dimethylacetal was added through the fractionating head. After the addition of the chloroacetal, the head temperature dropped rapidly from 130° to 89°. The product was collected; yield: 18.6 g (55.1%); b.p. 89-93° (lit. rep. 50%).

¹H NMR (60 MHz, CDCl₃): δ 3.08 (s, 2H), 3.57 (s, 6H).

¹³C NMR (CDCl₃): δ 54.14, 55.11, 167.07.

IR (neat): 3144 (w), 3008 (m), 2946 (m), 2840 (m), 2158 (w), 2044 (w), 1900 (w), 1842 (w), 1744 (m), 1648 (s), 1456 (s), 1381 (m), 1295 (s), 1195 (m), 1176 (m), 1128 (m), 1081 (m), 1056 (m), 1030 (s), 970 (w), 918 (w), 890 (m), 872 (m), 840 (w), 828 (w), 720 (m) cm⁻¹.

1,4-Dioxene (3)³²

In a 400 ml glass cylinder was charged 12.0 g of technical grade 9,10-phenanthrenequinone and 300 ml of dioxane. Nitrogen was bubbled through this mixture for one hour, then the solution was irradiated by a 350 nm UV lamp apparatus for 93 hours. The excess dioxane was removed by a rotatory evaporator, the last traces of dioxane were removed at 0.5 mm Hg until the odor of dioxane was not detected. The crude product was collected; yield: 14.6 g.

A 25 ml round-bottomed flask containing all the crude product was attached to a micro short-path still apparatus and immersed in an oil bath heated to 250°. Within a few minutes, rapid distillation began. The product was collected; yield: 3.96 g (93.0%); b.p. 90-92°.

^1H NMR (60 MHz, CDCl_3): δ 4.05 (s, 4H), 5.94 (s, 2H).

^{13}C NMR (CDCl_3): δ 64.62, 126.91.

IR (neat): 3090 (w), 2977 (m), 2930 (m), 2878 (m), 2020 (w), 1650 (s), 1456 (m), 1391 (w), 1370 (w), 1328 (w), 1268 (s), 1240 (m), 1122 (s), 1064 (s), 951 (m), 894 (s), 871 (m), 850 (m), 802 (m), 737 (s) cm^{-1} .

1-Diethylamino-1,3-butadiene (4)³³

In a 250 ml three-necked round-bottomed flask fitted with a thermometer, an addition funnel, and a mechanical stirrer were placed 45 g (0.615 mole) of diethylamine and 12 g of anhydrous potassium carbonate. The mixture was stirred and cooled to -10° in an ice-salt cooling bath. To the mixture was added 21 g (0.300 mole) of crotonaldehyde in 30 ml of benzene while the reaction mixture was kept at -5° to -10°. Then the mixture was stirred for one hour at 0°

and 4 hours at 20°; the liquid layer was decanted from the potassium carbonate; 0.2 g of 9,10-phenanthrenequinone was added and the solution was fractionally distilled at the reduced pressure. The product was collected; yield: 21.3 g (56.7%); b.p. 70-74 at 20 mm Hg (lit. rep. 60.9%).

^1H NMR (60 MHz, CDCl_3): δ 1.08 (t, 6H, $J = 7.2\text{Hz}$), 3.05 (q, 4H, $J = 7.2\text{ Hz}$), 4.30-5.26 (m, 3H), 5.33-6.61 (m, 2H).

^{13}C NMR (CDCl_3): δ 12.96, 44.93, 98.15, 103.32, 137.39, 141.33.

IR (neat): 3079 (w), 3038 (w), 2962 (m), 2930 (m), 2862 (m), 1630 (s), 1461 (w), 1450 (w), 1420 (m), 1390 (m), 1374 (m), 1360 (m), 1300 (w), 1280 (w), 1250 (m), 1205 (m), 1158 (m), 1110 (m), 990 (m), 951 (w), 922 (m), 843 (m), 814 (w), 770 (w), 646 (m) cm^{-1} .

1,1,3-Triethoxy butane (5)³⁴

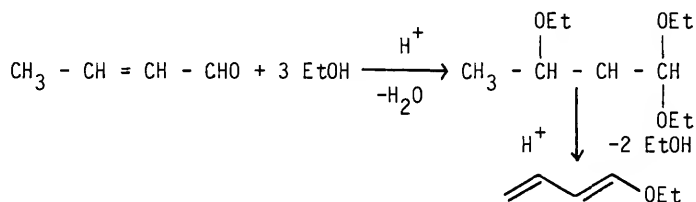
In a 2000 ml three-necked round-bottomed flask equipped with a thermometer, a gas inlet tube, and a water-cooled condenser, the top of which was connected to a mercury trap were placed 600 g (13.02 mole) of absolute alcohol, 300 g (4.28 mole) of crotonaldehyde, and 15 g of concentrated sulfuric acid. The solution was stirred and heated to 50° for 16 hours under a nitrogen atmosphere. After the given reaction time, the solution was cooled to room temperature, and 12.2 g of sodium hydroxide was added in as little water as possible. Then the mixture of ethyl alcohol, crotonaldehyde, and water was distilled off at 40° and 90 mm Hg. The residue was fractionated to yield product; yield: 280.9 g (34.5%); b.p. 75-77° at 10 mm Hg (lit. rep. 31.9-36.9%).

^1H NMR (60 MHz, CDCl_3): δ 1.20 (m, 12H), 1.76 (m, 2H), 3.55 (m, 7H), 4.68 (q, 1H).

^{13}C NMR (CDCl_3): δ 15.06, 15.30, 19.69, 41.08, 60.82, 61.21, 63.35, 71.49, 100.39.

IR (neat): 2978 (s), 2930 (m), 2878 (m), 1481 (w), 1443 (m), 1374 (m), 1342 (m), 1298 (w), 1278 (w), 1239 (w), 1120 (s), 1100 (s), 1060 (s), 1002 (m), 974 (m), 944 (w), 848 (w), 796 (w) cm^{-1} .

1-Ethoxy-1,3-butadiene (6)³⁵



In a 300 ml three-necked round-bottomed flask equipped with a dropping funnel, a thermometer, and a 1.8 cm diameter, 15 cm length glass tube wrapped with a heating tape, the top of which was connected to a distillation apparatus was placed 76.6 g of 1,1,3-triethoxybutane. To the liquid, heated to boiling, was added dropwise a 38.4 g portion of the triether containing 0.07 g of phosphoric acid. During this period, the 1-ethoxy-1,3-butadiene formed was allowed to distill constantly with the ethanol vapor as carrier. When the addition of this solution was over, an additional 38.4 g of triether was supplied, and the whole system was subjected to distillation. The rate of removal of the 1-ethoxy-1,3-butadiene and ethanol vapors was adjusted so that the vapor phase maintained

its temperature at 110-120°. Several drops of triethanolamine was added to the receiver as an inhibitor. The distillate collected was extracted twice with an equal volume of water, followed by drying over anhydrous sodium sulfate. Distillation of this layer under reduced pressure gave pure trans-1-ethoxy-1,3-butadiene, 27.1 g (34.3%); b.p. 58-60° at 105 mm Hg.

^1H NMR (60 MHz, CDCl_3): δ 1.26 (t, 3H, $J = 7.2$ Hz), 3.76 (q, 2H, $J = 7.2$ Hz), 4.64-6.73 (m, 5H).

^{13}C NMR (CDCl_3): δ 14.52, 65.06, 107.02, 111.02, 133.44, 150.69.

IR (neat): 3079 (w), 3041 (w), 2970 (m), 2921 (m), 2868 (m), 1688 (w), 1636 (s), 1598 (m), 1472 (w), 1434 (w), 1412 (w), 1388 (m), 1330 (m), 1295 (w), 1242 (w), 1188 (s), 1162 (m), 1124 (m), 1103 (m), 1018 (m), 988 (m), 910 (m), 874 (m), 850 (w), 812 (w), 650 (w), 630 (m) cm^{-1} .

Ethyl Sorbate (7)

In a 1000 ml three-necked round-bottomed flask equipped with a mechanical stirrer and a distillation apparatus were placed 112.1 g (1.0 mole) of sorbic acid, 180 ml of absolute alcohol, 90 ml of toluene, and 2 ml of concentrated sulfuric acid. The mixture was stirred and heated on an oil bath. An azeotropic mixture of alcohol, toluene, and water began to distill at 75°. Distillation was continued until the thermometer in the neck of the flask rose to 78°, when further heating was suspended. The distillate was collected in a 500 ml flask containing 75 g of anhydrous potassium carbonate. It was well shaken, filtered, and returned to the distilling flask. The

flask was again heated until the temperature rose to 78-80°. When distillation was discontinued, the residual liquid was poured into a 500 ml round-bottomed flask, and distilled under vacuum. The product was collected; yield: 110.8 g (79.1%); b.p. 85° at 20 mm Hg.

^1H NMR (60 MHz, CDCl_3): δ 1.27 (t, 3H, $J = 7.2$ Hz), 1.85 (d, 3H, $J = 5.4$ Hz), 4.18 (q, 2H, $J=7.2$ Hz), 5.61-6.52 (m, 3H), 7.03-7.53 (m, 1H).

^{13}C NMR (CDCl_3): δ 14.3, 18.6, 60.1, 119.1, 129.8, 139.1, 144.8, 167.3.

IR (neat): 3200 (m), 2980 (m), 2940 (m), 2910 (m), 2876 (w), 1710 (s), 1642 (s), 1618 (s), 1446 (m), 1390 (m), 1368 (s), 1327 (s), 1303 (s), 1260 (s), 1240 (s), 1218 (m), 1188 (s), 1138 (s), 1086 (m), 1036 (s), 998 (s), 948 (w), 922 (m), 868 (m), 798 (m), 740 (w), 710 (w), 690 (w) cm^{-1} .

Ethyl Muconate (8)³⁶

In a 100 ml round-bottomed flask fitted with a reflux condenser attached to a drying tube containing calcium chloride were placed 4.0 g of muconic acid, 40 ml of absolute alcohol, and 1 ml of concentrated sulfuric acid. The solution was refluxed for 24 hours. After the given reaction time, the reaction mixture was evaporated by a rotatory evaporator, and the crude residue was extracted with ether. The ether solution was washed with the 3% potassium carbonate solution to remove the unreacted muconic acid, the extract was dried, filtered, and evaporated. Recrystallization from methanol yielded 2.17 g (38.9%) of pure product, m.p. 61-63° (lit. rep. 63-64°).

^1H NMR (100 MHz, CDCl_3): δ 1.32 (t, 6H, $J = 7.2$ Hz), 4.24 (q, 4H, $J = 7.2$ Hz), 6.19 (dd, 2H, $J = 11.6, 3.0$ Hz), 7.31 (dd, 2H, $J = 11.6, 3.0$ Hz).

^{13}C NMR (CDCl_3): δ 14.17, 60.80, 128.37, 140.71, 165.87.

IR (neat): 3064 (w), 2979 (m), 2938 (w), 2908 (w), 1696 (s), 1610 (s), 1475 (w), 1465 (w), 1441 (w), 1386 (w), 1367 (m), 1310 (s), 1250 (s), 1158 (s), 1088 (m), 1020 (s), 858 (s), 810 (w), 740 (m), 714 (m), 690 (m) cm^{-1} .

2,4-Pentadienoic Acid (9)^{37,38}

Procedure A. In a 500 ml three-necked round-bottomed flask equipped with a constant pressure dropping funnel, a mechanical stirrer, and a thermometer were placed 90 g (0.865 mole) of malonic acid and 200 g (2.528 mole) of pyridine. The solution was stirred and cooled in an ice-salt bath. To the solution was added dropwise 60 g (1.070 mole) of acrolein. The mixture became yellow and deposited a very viscous oil. After 3 hours, the temperature was raised to 35-40° where it was kept for 5 hours during which the oil dissolved with evolution of carbon dioxide. The solution was acidified and extracted with ether. Upon removal of the ether, the acid was recovered as pale yellow crystals, 18.7 g (22.1%) (lit. rep. 30%). Pure acid was obtained by recrystallization from petroleum ether, m.p. 67-69° (lit. rep. 72°).

Procedure B. In a 500 ml four-necked round-bottomed flask equipped with a mechanical stirrer, an addition funnel, a thermometer, and a water-cooled condenser attached to a drying tube containing calcium chloride were placed 75 g (0.721 mole) of malonic

acid, 105 ml (1.298 mole) of pyridine, and 0.3 g of hydroquinone. The solution was heated to 50°, then 45.3 g (0.808 mole) of acrolein was added dropwise with stirring, and the temperature was maintained at 50° for 2 hours, and then at 80° for further 2 hours. The reaction mixture was poured on to ice, acidified, and the acid was extracted into dichloromethane. Upon removal of the solvent, the acid was recovered as pale yellow crystals, 34.3 g (48.5%) (lit. rep. 56%). The pure acid was obtained by recrystallization from the petroleum ether, m.p. 68-70° (lit. rep. 72°).

^1H NMR (60 MHz, CCl_4 -TMS): δ 5.44-7.66 (m, 5H), 12.26 (s, 1H).

^{13}C NMR ($\text{DMSO}-d_6$): δ 123.13, 125.81, 134.88, 144.29, 167.34.

IR (KBr): 3300-2500 (m, br), 1700 (s), 1630 (m), 1598 (m), 1430 (m), 1402 (m), 1308 (m), 1278 (s), 1216 (m), 1158 (m), 1007 (m), 964 (w), 928 (m), 864 (w) cm^{-1} .

Methyl 2,4-pentadienoate (10)^{38,39}

Procedure A. In a 50 ml beaker equipped with a mechanical stirrer was placed 5.0 g (0.051 mole) of 2,4-pentadienoic acid in 14.2 ml of 3.5 N aqueous ammonia solution. To this solution was added a solution of 9.5 g of silver nitrate in 9.0 ml of water. The precipitated silver salt was filtered, washed by deionized water, and dried in a vacuum oven at 45°. The yield was 8.48 g.

In a 100 ml round-bottomed flask equipped with an ice-water cooled condenser were placed all the silver salt, 5.88 g of methyl iodide, and 60 ml of dry ether. The solution was refluxed for 3 hours. The filtrate was fractionally distilled to give the product, 1.0 g (17.5%); b.p. 50° at 20 mm Hg.

Procedure B. In a 250 ml round-bottomed flask were placed 66.5 g (0.678 mole) of 2,4-pentadienoic acid, 110 ml of methanol, and 1.35 g of concentrated sulfuric acid. The mixture was allowed to stand overnight, and was then refluxed for 3 hours. The mixture was treated with water and extracted with ether. The extract was dried over anhydrous sodium sulfate. Finally, the ether was removed and the ester was purified by fractional distillation, 24.7 g (32.5%) (lit. rep. 70%); b.p. 50-52° at 20 mm Hg.

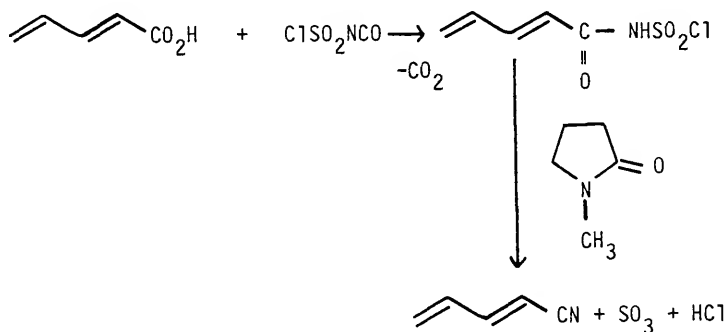
^1H NMR (60 MHz, CDCl_3): δ 3.76 (s, 3H), 5.40-7.56 (m, 5H).

^{13}C NMR (CDCl_3): δ 51.13, 121.55, 125.15, 134.51, 144.50, 166.77.

IR (neat): 3088 (w), 3050 (w), 3000 (m), 2950 (m), 2900 (w), 2840 (w), 1850 (w, br), 1716 (s), 1642 (s), 1600 (s), 1490 (w), 1435 (s), 1417 (m), 1370 (w, br), 1310 (s), 1268 (s), 1205 (s), 1146 (s), 1035 (m), 1008 (s), 961 (m), 928 (m), 868 (m), 742 (w), 720 (m), 705 (w) cm^{-1} .

1-Cyano-1,3-butadiene (11)^{38,40}

Procedure A.



Pyrolysis of crotonaldehyde cyanohydrine benzoate at $575 \pm 10^\circ$, was conducted by dropping the ester at a rate of one drop per 1.4 second through a vertical 2.4 cm diameter, 31 cm length quartz tube packed with a ceramic beads. To minimize dimerization of the trans-1-cyano-1,3-butadiene, the volatile components of the pyrolysate were distilled at 1 mm Hg in a distillation apparatus with a dry ice condenser with the receiver immersed in a dry ice-acetone cooling bath. Utilizing 56.5 g of the ester, the yield of the crude mixed dienes was 12.7 g (57.2%); b.p. $57-60^\circ$ at 32 mm Hg (lit. rep. 70%).

^1H NMR (60 MHz, CDCl_3): δ 5.27-7.33 (m, 5H).

^{13}C NMR (CDCl_3): δ 99.42, 117.35, 126.27, 133.73, 150.20 (trans-isomer).

^{13}C NMR (CDCl_3): δ 97.95, 115.70, 126.42, 132.41, 149.23 (cis-isomer).

IR (neat): 3220 (w), 3092 (w), 3048 (w), 3010 (w), 2218 (m), 1860 (w, br), 1622 (m), 1588 (m), 1418 (w), 1290 (w), 1258 (w), 1002 (m), 955 (m), 930 (m), 832 (m) cm^{-1} (trans-isomer only).

IR (neat): 3220 (w), 3092 (w), 3048 (w), 3010 (w), 2218 (m), 1860 (w, br), 1622 (m), 1588 (m), 1572 (m), 1428 (w), 1418 (w), 1358 (w), 1290 (w), 1258 (w), 1228 (w), 1002 (m), 955 (m), 930 (m), 832 (m), 774 (m), 665 (m) cm^{-1} (mixture of both isomers).

Crotonaldehyde Cyanohydrin Benzoate (12)⁴⁰

In a 1000 ml three-necked round-bottomed flask equipped with a thermometer, an addition funnel, and a magnetic stirring bar were placed 50 g of crotonaldehyde and 150 ml of benzene. The solution was cooled to -10° in an ice-salt bath. To the solution was slowly

added 100 g of benzoyl chloride, then added dropwise was 61.9 g of potassium cyanide while the reaction mixture was kept at the same temperature. After the cyanide had been added the mixture was stirred for 2 hours at -10° and then was allowed to warm to room temperature. The organic layer was separated, washed with two 25 ml portions of 5% sodium carbonate solution, and dried over anhydrous magnesium sulfate. After distillation of the benzene, the residue was fractionated through a Vigreux column. The product was collected, 110.9 g (77.3%); b.p. $123-125^{\circ}$ at 1 mm Hg.

^1H NMR (60 MHz, CDCl_3): δ 1.84 (d, 3H, $J = 6.0$ Hz), 5.44-6.62 (m, 3H), 7.24-7.71 (m, 3H), 7.93-8.20 (m, 2H).

^{13}C NMR (CDCl_3): δ 17.50, 61.75, 115.65, 121.30, 128.17, 128.42, 129.78, 133.78, 135.53, 164.39.

IR (neat): 3060 (w), 3038 (w), 2972 (w), 2942 (m), 2920 (m), 2858 (w), 1730 (s), 1670 (m), 1598 (m), 1572 (m), 1490 (w), 1450 (s), 1379 (m), 1316 (s), 1300 (s), 1255 (s), 1178 (s), 1142 (m), 1088 (s), 1065 (s), 1023 (s), 962 (s), 930 (m), 802 (w), 710 (s), 682 (m) cm^{-1} .

1-Carbethoxy-1-cyano-1,3-butadiene (13)⁴¹

In a 300 ml round-bottomed flask equipped with a magnetic stirring bar and an addition funnel were placed 25.0 g of zinc chloride, 100 ml of dioxane, and 33.9 g (0.30 mole) of ethyl cyanoacetate. To the solution was added dropwise 25 ml (0.375 mole) of acrolein at room temperature. After 3 hours, the reaction solution was diluted with 250 ml petroleum ether, extracted three times with 500 ml portions of cold dilute hydrochloric acid, then

dried and concentrated. The product was collected, 28.2 g (62.3%), m.p. 37-38° (lit. rep. 68%, m.p. 39-40°).

^1H NMR (60 MHz, CDCl_3): δ 1.37 (t, 3H, $J = 7.2$ Hz), 4.35 (q, 2H, $J = 7.2$ Hz), 6.07 (m, 2H), 6.97 (m, 1H), 7.86 (d, 1H, $J = 5.5$ Hz).

^{13}C NMR (CDCl_3): δ 13.79, 62.18, 106.73, 113.36, 131.68, 133.83, 154.93, 161.36.

IR (thin film): 3049 (m), 2262 (m), 1946 (w), 1709 (s), 1629 (s), 1592 (s), 1473 (m), 1443 (m), 1428 (w), 1401 (w), 1374 (m), 1348 (m), 1321 (m), 1297 (s), 1250 (s), 1188 (m), 1068 (s), 1015 (m), 993 (m), 960 (m), 859 (w), 833 (w), 761 (m), 733 (w) cm^{-1} .

1,3-Butadienyl trimethyl ammonium chloride (14)⁴²

In a 450 ml autoclave were placed 24.7 g of trimethylamine, 18.9 g of trans-1,4-dichloro-2-butene, and 180 ml of benzene. The solution was heated to 100° for one hour in the closed system. After the given reaction time, the solution was cooled to room temperature. The product was filtered, washed, then dried in a vacuum oven at 50° to yield 25.9 g, 1,4-bis(trimethylammonium)-2-butene chloride. This salt was added with 52 ml 10% NaOH and 105 ml water, then the mixture was distilled until the condensate was neutral. The residual solution was neutralized with 10% hydrochloric acid, decolorized, filtered, and evaporated in a rotatory evaporator under reduced pressure. The residue was extracted with chloroform. The extract was dried over anhydrous sodium sulfate. Finally, the chloroform was removed and product was obtained 3.54 g (15.9%).

^1H NMR (60 MHz, CDCl_3): δ 3.67 (s, 9H), 5.37-7.45 (m, 5H).

^{13}C NMR (CDCl_3): δ 53.95, 123.84, 125.79, 129.05, 137.04.

Copolymer Synthesis

All copolymers were synthesized by roughly the same method. Azobisisobutyronitrile (AIBN) was used as the initiator in the organic phase reactions; azobis(2-amidinopropane)hydrochloride (V-50) was used as the initiator in the aqueous phase reactions.

Pyrex polymerization tubes were charged with the prescribed quantities of freshly purified monomers, initiators, and solvents. The tubes were connected to a high vacuum line, degassed by several freeze-pump-thaw cycles, and sealed off under vacuum.

The monomers were polymerized by heating the sealed tubes at the prescribed temperature in a shaking water bath for a fixed period. At the end of the reaction time, the tubes were removed from the bath, cooled to -78° in a dry ice-isopropanol cooling bath in order to stop the reaction, and opened. The solution was then slowly added to a large excess of rapidly stirred precipitation solvent (petroleum ether was used unless otherwise noted). The polymers were purified by dissolving them in acetone and then precipitating from petroleum ether. After having been dried overnight in vacuum, the copolymers were weighed and analyzed.

The copolymerization conditions, yields and analysis data for the polymerizations of both diene-dienophile and diene-diene systems are shown in Tables 1-11.

TABLE 1

Conditions for the Polymerizations of Methyl 2,4-Pentadienoate (MPD) with Electron-Rich Dienophiles

Sample No.	Electro-rich dienophile	$m_T \times 10^2$ ^b	f_A ^c	$m_{AIBN} \times 10^4$ ^d	Vol. ^e (ml)	Time (Hr.)	Temp. (°C)
1	DOE	1.33	0.504	1.04(0.77%)	4	63	50
2	BVE	5.90	0.502	1.47(0.25%)	5	66	60
3	BVE	1.52	0.499		4	68	60
4	CEVE	1.11	0.495	0.43(0.39%)	2	64	50
5	-	1.64	1.000	0.82(0.50%)	3	66	60

^aAbbreviations used:

AN, acrylonitrile
 ATBD, 1-acetoxy-1,3-butadiene
 BTAC, 1,3-butadienyl trimethyl ammonium chloride
 BVE, n-butyl vinyl ether
 CBD, 1-cyano-1,3-butadiene
 CCB, 1-carbethoxy-1-cyano-1,3-butadiene
 CEVE, 2-chloroethyl vinyl ether
 DABD, 1-diethylamino-1,3-butadiene
 DEM, diethyl muconate
 DHP, 2,3-dihdropyran
 DOE, 1,4-dioxene
 EA, ethyl acrylate
 EBD, 1-ethoxy-1,3-butadiene
 ECA, ethyl α -cyanoacrylate
 ESB, ethyl sorbate
 EVE, ethyl vinyl ether
 FN, fumaronitrile
 KEA, ketene, diethylacetal
 KMA, ketene, dimethylacetal
 MPD, methyl 2,4-pentadienoate
 PA, potassium acrylate
 PPD, potassium 2,4-pentadienoate
 TSD, 1-trimethylsilyloxy-1,3-butadiene
 TVAB, trimethyl vinyl ammonium bromide

^bTotal moles of monomers.^cMole fraction of acceptor in the initial feed.^dMoles of AIBN (mole % AIBN based on m_T).^eVolume of benzene that was polymerized.

TABLE 2
Yields and Analysis Data for Polymers in Table 1

Sample No.	Yield		Analysis		[η] dl/g
	Grams	%	C, %	H, %	
1	0.150	20.0			
2	1.698	51.3	64.03	7.30	
3	0	0			
4	0.222	35.9			
5	0.802	43.6			0.24 ^a

^aIntrinsic viscosity was measured in tetrahydrofuran at 25°C.

TABLE 3

Conditions for the Polymerizations of 1-Carbethoxy-1-cyano-1,3-butadiene (CCB)
with Electron-Rich Dienophiles

Sample No.	Electron-rich ^a Dienophile	$m_1 \times 10^2$ ^b	f_A ^c	$m_{AIBN} \times 10^4$ ^d	$m_{BA} \times 10^4$ ^e	$m_{HQ} \times 10^4$ ^f	Vol. g (ml)	Time (Hr.)	Temp. (°C)
6	DOE	0.964	0.499	0.55(0.57%)			8	48	50
7	BVE	3.600	0.500	0.91(0.25%)	2.4		7	43	60
8	BVE	2.114	0.499				8	68	60
9	BVE	2.508	0.498		125.0		12	66	60
10	8VE	1.291	0.499		0.8		4	68	60
11	BVE	1.313	0.497			65.6	8	68	60
12	-	1.210	1.000	0.61(0.50%)	1.6		6	43	60
13	-	0.942	1.000		1.1		4	43	60
14	CEVE	2.664	0.500	0.97(0.37%)	1.6		7	87	50
15	KEA	1.050	0.500	0.49(0.46%)			8	48	50
16	DHP	0.895	0.498	0.43(0.48%)			8	48	50
17	EVE	1.031	0.500	0.52(0.51%)			8	48	50

^{a-d}See Table 1 for footnote descriptions.

^eMoles of benzoic acid.

^fMoles of hydroquinone.

^gVolume of benzene that was polymerized.

TABLE 4
Yields and Analysis Data for Polymers in Table 3

Sample No.	Yield		Analysis			[η] dl/g
	Grams	%	C, %	H, %	N, %	
6	0.54	74.9				
7	2.21	81.5	63.66	6.19	9.06	0.38 ^a
8	1.24	87.9				
9	0.50	26.5				
10	0.74	76.1				
11	0	0				
12	0.36	19.7	63.72	6.23	9.11	
13	0	0				
14	1.48	73.6				
15	0.52	66.1				
16	0.52	77.3				
17	0.67	86.4				

^aIntrinsic viscosity was measured in tetrahydrofuran at 25°C.

TABLE 5

Conditions for the Copolymerizations of Acrylonitrile (AN)
with Electron-Rich Dienes

Sample No.	Electro-rich ^a diene	$m_T \times 10^2$ ^b	f_A ^c	$m_{AIBM} \times 10^4$ ^d	Vol. ^e (ml)	Time (Hr.)	Temp. (°C)
18	EBD	2.75	0.500	0.99(0.30%)	4	71	60
19	DABD	1.46	0.500	1.40(0.96%)	5	65	60
20	ATBD	3.08	0.500	0.66(0.22%)	4	67	60
21	TSBD	2.99	0.499	0.60(0.20%)	4	67	60
22	EBD	4.25	0.502		8	70	60
23	DABD	3.66	0.500		4	69	60
24	ATBD	1.82	0.503		4	67	60
25	TSBD	1.49	0.502		4	67	60

^{a-e}See Table 1 for footnote descriptions.

TABLE 6
Yields and Analysis Data for Copolymers in Table 5

Sample No.	Yield		Analysis				[η] dl/g
	Grams	%	C, %	H, %	N, %	F _A ^a	
18	0.95	37.9	71.6	8.7	9.2	0.498	0.155 ^b
19	0.10	7.7	73.9	10.2	15.5	0.485	0.459 ^c
20	1.00	39.3	64.3	7.0	6.4	0.405	0.347 ^c
21	0.70	24.0	61.4	9.0	6.9	0.488	0.254 ^b
22	0.40	12.5	70.6	8.6	8.7	0.477	
23	0	0					
24	0.20	13.3	64.8	6.8	6.1	0.391	
25	0.10	6.9					

^aMole fraction of acceptor in the copolymer calculated from results of elemental analysis.

^bIntrinsic viscosity was measured in toluene at 25°C.

^cIntrinsic viscosity was measured in tetrahydrofuran at 25°C.

TABLE 7

Conditions for the Copolymerizations of Electron-Rich Dienes (ERD)
with Electron-Poor Dienes (EPD)

Sample No.	EPD ^a	ERD ^a	$m_T \times 10^2$ ^b	f_A^c	$m_{ATBN} \times 10^5$ ^d	Vol. ^e (ml)	Time (Hr.)	Temp (°C)
26	CBD	EBD	2.65	0.500	5.2(0.20%)	8	64	50
27	CBD	ATBD	2.56	0.500	5.5(0.21%)	8	64	50
28	CBD	ATBD	0.46	0.495	1.2(0.26%)	1.3	70	60
29	MPD	EBD	2.02	0.751	6.1(0.30%)	4	81	60
30	MPD	EBD	1.93	0.500	4.9(0.25%)	4	81	60
31	MPD	EBD	2.88	0.248	8.5(0.30%)	4	81	60
32	MPD	EBD	1.67	0.498		4	81	60
33	MPD	EBD	2.84	0.500	5.7(0.20%)	8	70	50
34	MPD	ATBD	2.64	0.500	5.3(0.20%)	8	70	50
35	MPD	ATBD	2.33	0.503	20.1(0.86%)	6	63	50
36	CCB	ATBD	3.21	0.501	13.4(0.42%)	8	87	50
37	MPD	DABD	2.37	0.498	18.9(0.80%)	6	63	50
38	ESB	DABD	4.04	0.500	36.5(0.90%)	10	63	60
39	DEM	DABD	0.80	0.500	11.6(1.45%)	10	63	60
40	ESB	ATBD	2.73	0.500	7.3(0.27%)	5	92	60

^{a-e}See Table 1 for footnote descriptions.

TABLE 8
Yields and Analysis Data for Copolymers in Table 7

Sample No.	Yield		Analysis				$[\eta]$ dl/g
	Grams	%	C, %	H, %	N, %	F_A^a	
26	0.24	10.3	74.1	7.9	10.6	0.648	0.84 ^b
27	0.10	4.1	71.1	6.9	10.9	0.694	1.03 ^b
28	0.04	9.1					
29	1.30	59.4	65.2	7.7		0.873	
30	0.70	34.6	66.0	8.0		0.769	0.29 ^c
31	0.60	20.5	67.3	8.4		0.621	
32	0.30	17.1	65.6	7.8		0.819	
33	0.49	16.4					
34	0.60	20.3					
35	0.37	14.1					
36	0.79	18.7					
37	0	0					
38	0	0					
39	0	0					
40	0.42	12.3					

^aMole fraction of acceptor in the copolymer calculated from results of elemental analysis.

^bIntrinsic viscosity was measured in tetrahydrofuran at 25°C.

^cIntrinsic viscosity was measured in toluene at 25°C.

TABLE 9
Conditions for the Polymerizations of Some Electron-Rich Monomers (ERM)
with Some Electron-Poor Monomers (EPM)

Sample No.	ERM ^a	EPM ^a	$\eta_{sp} \times 10^2$ ^b	f_A ^c	$m_{AIBN} \times 10^4$ ^d	$m_{BA} \times 10^4$ ^e	$m_{HQ} \times 10^4$ ^f	Vol. g (ml)	Time (Hr.)	Temp. (°C)
41	BVE	CBD	5.66	0.498	1.52(0.27%)			4	92	60
42	-	CBD	0.98	1.000	0.67(0.68%)			2	92	60
43	KEA	ESB	4.00	0.500	4.00(1.00%)			25	48	60
44	-	ESB	5.61	1.000	11.20(2.00%)			25	48	60
45	EBD	-	1.04	1.000	0.54(0.52%)			4	120	60
46	EBD	AN	5.84	0.500			2.82	4	92	60
47	EBD	ECA	2.92	0.306	1.10(0.38%)	1.72		4	65	60
48	EBD	ECA	1.97	0.500	0.66(0.34%)	1.39		4	111	60
49	EBD	FN	2.08	0.500	0.52(0.25%)			4	0.5	60
50	DABD	-	1.97	1.000	1.04(0.53%)			3	64	60
51	DABD	EA	2.90	0.500				3	66	60
52	DABD	EA	4.89	0.524	1.58(0.32%)			6	66	60

^{a-d}See Table 1 for footnote descriptions.

^eMoles of benzoic acid.

^fMoles of hydroquinone.

^gVolume of benzene that was polymerized.

TABLE 10
Yields and Analysis Data for Polymers in Table 9

Sample No.	Yields		Analysis			F_A^a mole-%
	Grams	%	C, %	H, %	N, %	
41	0.63	28.3				
42	0.12	15.2				
43	0					
44	0					
45	0					
46	0					
47	0					
48	0.22	10.0	58.4	6.0	10.2	88.3
49	1.24	67.5	67.5	6.9	15.6	49.3
50	0					
51	0					
52	0					

^aMole fraction of acceptor in the copolymer calculated from the results of elemental analysis.

Copolymerizations in Aqueous Phase

Acetone was used as precipitation solvent for those copolymerizations which were carried out in aqueous phase. The conditions and results of polymerizations of water-soluble monomers are shown in Table 11.

TABLE 11
Conditions and Results of Polymerizations
of Water-Soluble Monomers

Sample No.	Acceptor ^a	Donor ^a	$m_T \times 10^2$ ^b	f_A ^c	$m_{V-50} \times 10^4$ ^d	Vol ^e (ml)	Time (Hr.)	Yield (%)
53	TVAB	PA	0.848	0.494	0.57(0.49%)	2	20	48.8
54	TVAB	PA	0.627	0.493	0.30(0.47%)	3	22	60.8
55	TVAB	PPD	1.426	0.500	0.63(0.44%)	4	22	67.7
56	BTAC	PA	0.163	0.500	0.08(0.50%)	2	40	0

^{a-c}See Table 1 for footnote descriptions.

^dMoles of V-50 (mole % V-50 based on m_T).

^eVolume of water that was polymerized.

Monomer Reactivity Ratios

In order to determine the monomer reactivity ratios of acrylonitrile and 1-ethoxy-1,3-butadiene, radial copolymerizations were carried out at 60°C with the use of AIBN as initiator; total monomer and initiator concentrations were kept constant at 5.5 M and 1.30×10^{-2} M, respectively (Table 12).

TABLE 12

Conditions, Yields and Analysis Data for the Copolymerizations
of Acrylonitrile (AN) with 1-Ethoxy-1,3-butadiene (EBD)

EBD in feed (mole-%)	Time (Hr.)	Copolymer Produced				EBD (mole-%)
		Yield %	Analysis			
			C, %	H, %	N, %	
9.0	20	86.3	68.1	6.4	20.9	12.6
16.7	62	76.1	68.5	6.7	20.0	14.9
27.7	13	21.4				
27.7	4	7.3			9.4	49.6
37.6	16	19.2				
37.9	7	10.0			9.2	50.2
50.3	32	18.2	71.5	8.7	9.1	50.6
63.1	40	10.4			8.6	52.7
73.3	52	9.4			8.3	54.0
83.5	90	5.6	71.1	8.8	7.5	57.5

In order to determine the monomer reactivity ratios of acrylonitrile and 1-diethylamino-1,3-butadiene, radical copolymerizations were carried out at 60°C with the use of AIBN as initiator; total monomer and initiator concentrations were kept constant at 5.8 M and 1.4×10^{-2} M, respectively (Table 13).

TABLE 13

Conditions, Yields and Analysis Data for the Copolymerizations of Acrylonitrile (AN) with 1-Diethylamino-1,3-butadiene (DABD)

DABD in feed (mole-%)	Time (Hr.)	Copolymer Produced				DABD (mole-%)
		Yield %	Analysis			
			C, %	H, %	N, %	
23.3	9	6.1	72.1	9.0	18.3	32.4
27.9	15	6.0	71.7	9.0	18.2	33.0
34.3	20	5.9	72.6	9.2	17.8	35.9
41.2	22	5.3	71.9	9.8	16.6	43.5
49.9	45	7.4	73.4	10.0	15.7	50.2
59.0	62	2.7	73.1	10.6	15.1	55.6
68.5	72	0				
75.2	146	0				

Copolymer Characterization

The resulting polymers were analyzed by IR, ^1H NMR and ^{13}C NMR methods.

NMR Techniques

Since the greater spectral simplicity resulting from the lacking of coupling and greater spectral width, the ^{13}C NMR technique has been regarded as a more powerful tool than the ^1H NMR technique in analyses of copolymers.

The Jeol-FX-100 instrument has been used for taking the ^{13}C NMR spectra of the resulting copolymers. However, this instrument has limited space in the computer memory system for data storage; the computer word length would overflow before an adequate signal-to-noise ratio was attained. This problem was overcome by using the frequency domain (or block) averaging technique.⁴³ According to this method, the free induction decay is averaged for a certain number of scans such that Fourier transformed, phase corrected, stored in a separate area of memory, and acquisition repeated after zeroing the data area. After a second block of data is Fourier transformed, this is added to the first result and the process is repeated until a sufficient signal-to-noise ratio is obtained.

The INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) technique provides an alternative to the off-resonance experiment for assignment of quaternary, methine, methylene and methyl carbons. This approach was proposed by Ernst⁴⁴ and Doddrell,⁴⁵ respectively. It overcomes two of the disadvantages of the off-resonance experiment, i.e., overlap of resonance lines and decreased

sensitivity. In the case of delay time (Δ) is $1/4J$, all of the protonated carbons exhibit a positive signal intensity in the spectrum, while at $\Delta = 2/4J$, only methine carbons show maximum intensity with methyl and methylene carbons at minimum intensity and $\Delta = 3/4J$, methyl and methine carbons show positive intensity with methylene carbons 180° out of phase.

IR Spectroscopy

IR spectra were obtained either by using the KBr pellet technique or by coating a thin film on KBr plates. The abbreviations used below for the various monomer and comonomer pairs used to synthesize the polymers are the same as those used in Tables 1-11.

MPD-CEVE, 2983 (m), 2940 (m), 2907 (w), 2838 (w), 1730 (s), 1650 (m), 1430 (m), 1360 (m), 1330 (m), 1308 (m), 1262 (m), 1220 (m), 1190 (m), 1156 (s), 1020 (m), 964 (s), 910 (w), 850 (w), 722 (w) cm^{-1} .

MPD, 2988 (m), 2942 (m), 2840 (m), 1725 (s), 1650 (m), 1432 (s), 1355 (m), 1330 (m), 1310 (m), 1262 (s), 1220 (m), 968 (s), 912 (m), 850 (w), 730 (s), 640 (w) cm^{-1} .

CCB, 2980 (m), 2930 (m), 2866 (w), 2226 (w), 1733 (s), 1622 (m), 1464 (m), 1442 (m), 1390 (m), 1368 (m), 1250 (s), 1156 (m), 1090 (m), 1070 (m), 1015 (m), 970 (m), 890 (w), 852 (m), 760 (m) cm^{-1} .

CCB-CEVE, 2979 (m), 2938 (m), 2900 (w), 2864 (w), 2350 (w), 2320 (w), 2241 (w), 2198 (w), 1738 (s), 1624 (m), 1465 (m), 1442 (m), 1388 (m), 1368 (m), 1295 (m), 1235 (s), 1158 (m), 1092

(m), 1019 (m), 968 (m), 912 (m), 854 (m), 760 (w), 730 (m),
668 (w), 645 (w) cm^{-1} .

CCB-BVE, 2979 (m), 2938 (m), 2902 (m), 2866 (m), 2242 (m), 2198
(w), 1735 (s), 1722 (m), 1622 (m), 1463 (m), 1442 (m), 1388
(m), 1368 (m), 1297 (m), 1235 (s), 1158 (m), 1092 (m), 1019
(m), 968 (m), 912 (m), 853 (m), 760 (w), 730 (m), 668 (w),
645 (w), 620 (w) cm^{-1} .

AN-EBD, 2978 (m), 2924 (m), 2868 (m), 2238 (m), 1648 (m), 1478 (w),
1442 (m), 1380 (m), 1348 (w), 1302 (m), 1245 (w), 1216 (w),
1168 (m), 1104 (s), 1040 (w), 972 (m), 938 (w), 850 (w), 806
(w), 754 (w), 729 (w) cm^{-1} .

AN-DABD, 3044 (w), 2962 (m), 2924 (m), 2862 (m), 2232 (m), 1722
(w), 1646 (s), 1448 (m), 1400 (m), 1374 (m), 1345 (m), 1295
(m), 1250 (m), 1214 (m), 1180 (m), 1169 (m), 1098 (m), 990
(w), 940 (m), 915 (w), 810 (w), 778 (m), 730 (m) cm^{-1} .

AN-ATBD, 3018 (m), 2926 (m), 2850 (w), 2238 (m), 1735 (s), 1670
(m), 1432 (m), 1370 (s), 1230 (s), 1085 (m), 1040 (m), 1020
(s), 970 (s), 936 (m), 754 (m), 662 (w) cm^{-1} .

AN-TSBD, 3100 (w), 2952 (m), 2857 (w), 2237 (w), 1651 (m), 1448
(m), 1406 (m), 1365 (w), 1251 (s), 1210 (m), 1165 (m), 1122
(m), 1075 (s), 970 (m), 930 (m), 850 (s), 751 (m), 688 (w),
642 (w) cm^{-1} .

CBD (mixtures of trans and cis isomers)-ATBD, 3020 (w), 2921 (m),
2859 (w), 2241 (m), 2221 (m), 1732 (s), 1673 (w), 1632 (w),
1438 (m), 1372 (m), 1237 (s), 1045 (m), 1020 (m), 969 (s),
913 (m), 758 (m), 731 (m), 645 (w) cm^{-1} .

CBD (trans isomer only)-ATBD, 3020 (w), 2920 (m), 2855 (w), 2239 (m), 2219 (m), 1732 (s), 1670 (m), 1629 (w), 1435 (m), 1370 (m), 1239 (s), 1038 (m), 968 (m), 759 (w) cm^{-1} .

CBD-EBD, 3040 (w), 2979 (m), 2928 (m), 2240 (w), 2221 (w), 1669 (w), 1649 (m), 1441 (m), 1372 (w), 1304 (w), 1204 (w), 1162 (m), 1104 (m), 1085 (m), 970 (s), 937 (w), 915 (w), 853 (w), 805 (w), 750 (w), 730 (m) cm^{-1} .

MPD-ATBD, 3000 (m), 2952 (m), 2842 (w), 1730 (s), 1652 (m), 1436 (s), 1372 (m), 1235 (s), 1160 (s), 1021 (m), 970 (s), 915 (m), 852 (w), 731 (m), 647 (w) cm^{-1} .

MPD-EBD, 3010 (w), 2962 (m), 2942 (m), 2840 (w), 1730 (s), 1646 (m), 1432 (m), 1355 (w), 1260 (m), 1218 (m), 1189 (m), 1155 (s), 1100 (m), 1076 (m), 1020 (m), 965 (s), 930 (w), 848 (w), 742 (w) cm^{-1} .

CCB-ATBD, 2980 (m), 2938 (m), 2845 (w), 2350 (w), 2228 (w), 1736 (s), 1670 (w), 1645 (w), 1622 (m), 1465 (m), 1442 (m), 1335 (m), 1270 (m), 1233 (s), 1154 (w), 1092 (m), 1020 (m), 968 (m), 935 (w), 916 (w), 854 (w), 762 (w), 728 (m), 645 (w) cm^{-1} .

ESB-ATBD, 2973 (m), 2928 (m), 2340 (w), 1732 (s), 1695 (m), 1670 (m), 1650 (w), 1434 (m), 1370 (m), 1234 (s), 1172 (m), 1155 (m), 1090 (m), 1020 (m), 969 (m), 934 (w), 852 (w), 762 (w) cm^{-1} .

CCB-EBD, 2978 (m), 2928 (m), 2898 (w), 2862 (w), 2223 (w), 1736 (s), 1620 (m), 1462 (m), 1442 (m), 1386 (m), 1366 (m), 1240

(s), 1156 (m), 1090 (m), 1019 (m), 969 (m), 910 (w), 852 (m), 760 (m), 728 (w), 645 (w) cm^{-1} .

CBD-BVE, 3041 (w), 2980 (w), 2920 (m), 2848 (w), 2238 (w), 2220 (m), 1628 (w), 1438 (m), 1355 (w), 1080 (w), 969 (s), 912 (m), 753 (w), 728 (m), 643 (w) cm^{-1} .

FN-EBD, 2979 (m), 2938 (m), 2880 (m), 2242 (m), 1669 (m), 1648 (m), 1480 (w), 1442 (m), 1398 (w), 1373 (m), 1330 (w, br), 1178 (m), 1105 (s), 1018 (w), 979 (m), 945 (w), 885 (w), 848 (w), 810 (w) cm^{-1} .

ECA-EBD, 2978 (m), 2930 (m), 2900 (m), 2862 (w), 2239 (w), 1745 (s), 1660 (w), 1465 (m), 1438 (m), 1380 (m), 1365 (m), 1250 (s), 1158 (m), 1100 (m), 1008 (m), 850 (m), 740 (w) cm^{-1} .

Several Diels-Alder adducts have been isolated from the copolymerizations of electron-rich dienes with electron-poor dienophiles. The spectral data of these compounds are shown below.

4-Cyano-3-ethoxycyclohexene

^1H NMR (60 MHz, CDCl_3): δ 1.22 (t, 3H, $J=7.2$ Hz), 2.70 (m, 4H), 2.82 (m, 1H), 3.63 (q, 2H, $J=7.2$ Hz), 4.00 (m, 1H), 5.53-6.10 (t, 2H).

^{13}C NMR (CDCl_3): δ 15.16 (t), 22.03 (t), 22.41 (t), 22.71 (t), 23.00 (t), 30.75 (d), 30.89 (d), 64.77 (t), 64.86 (t), 73.25 (d), 119.50 (s), 120.52 (s), 125.15 (d), 125.69 (d), 129.39 (d), 129.83 (d).

IR (neat): 3028 (m), 2968 (s), 2938 (s), 2882 (s), 2238 (m), 1742 (m), 1685 (w), 1648 (m), 1618 (w), 1480 (m), 1445 (m), 1432 (m), 1389 (m), 1369 (m), 1324 (m), 1290 (m), 1270 (m), 1227 (w), 1171 (m),

1090 (s), 1053 (m), 1020 (m), 980 (m), 940 (w), 915 (m), 890 (m), 868 (m), 835 (w), 814 (w), 795 (w), 768 (w), 756 (w), 722 (m), 679 (m), 652 (m) cm^{-1} .

4-Cyano-3-diethylaminocyclohexene

^1H NMR (60 MHz, CDCl_3): δ 1.07 (t, 6H, $J=7.2$ Hz), 2.09 (m, 4H), 2.60 (m, 5H), 3.60 (m, 1H), 5.46-6.10 (m, 2H).

^{13}C NMR (CDCl_3): δ 14.13, 14.28, 21.88, 23.49, 24.56, 25.53, 29.53, 30.26, 43.96, 44.40, 57.26, 54.48 120.91, 122.08, 126.57, 127.05, 128.52, 128.86.

IR (neat): 3022 (m), 2962 (s), 2928 (s), 2864 (m), 2840 (m), 2238 (m), 1642 (m), 1463 (m), 1449 (m), 1431 (m), 1379 (m), 1335 (m), 1300 (m), 1285 (m), 1262 (m), 1204 (m), 1180 (m), 1144 (m), 1110 (m), 1062 (s), 1032 (m), 980 (w), 959 (w), 931 (w), 902 (w), 870 (w), 778 (w), 764 (w), 720 (m), 668 (m) cm^{-1} .

4-Carbethoxy-3-diethylaminocyclohexene

^1H NMR (60 MHz, CDCl_3): δ 0.95 (t, 3H, $J=7.2$ Hz), 0.98 (t, 3H, $J=7.2$ Hz), 1.25 (t, 3H, $J=7.2$ Hz), 1.98 (m, 4H), 2.53 (m, 5H), 3.63 (m, 1H), 4.13 (q, 2H, $J=7.2$ Hz), 5.45-6.08 (m, 2H).

IR (neat): 3018 (m), 2964 (s), 2928 (s), 2900 (s), 2865 (m), 2810 (m), 2718 (m), 1732 (s), 1674 (m), 1643 (m), 1463 (m), 1447 (m), 1370 (s), 1335 (m), 1298 (s), 1259 (m), 1220 (s), 1202 (s), 1160 (s), 1100 (m), 1055 (s), 1035 (s), 978 (m), 962 (m), 932 (s), 910 (s), 882 (m), 863 (m), 842 (s), 794 (m), 766 (w), 752 (w), 732 (m), 689 (m), 645 (w) cm^{-1} .

4-Cyano-4-carbethoxy-3-ethoxycyclohexene

^1H NMR (60 MHz, CDCl_3): δ 1.12 (t, 3H, $J=7.2$ Hz), 1.33 (t, 3H, $J=7.2$ Hz), 2.23 (m, 4H), 3.58 (m, 2H), 4.30 (m, 4H), 5.73-6.27 (m, 2H).

^{13}C NMR (CDCl_3): δ 13.69 (q), 15.06 (q), 21.93 (t), 22.08 (t), 22.32 (t), 28.94 (t), 46.49 (s), 49.47 (s), 62.04 (t), 62.53 (t), 65.25 (t), 65.45 (t), 72.96 (d), 116.38 (s), 117.69 (s), 122.62 (d), 125.49 (d), 127.69 (d), 131.63 (d), 166.04 (s), 168.43 (s).

IR (neat): 3038 (w), 2978 (s), 2937 (m), 2898 (m), 2240 (w), 1750 (s), 1648 (w), 1464 (m), 1442 (m), 1431 (m), 1391 (m), 1368 (m), 1329 (m), 1312 (m), 1294 (m), 1240 (s), 1200 (s), 1170 (m), 1090 (s), 1062 (s), 1048 (s), 1020 (m), 969 (m), 934 (w), 880 (m), 853 (m), 803 (w), 769 (w), 733 (m), 721 (m), 632 (w) cm^{-1} .

4-Ethoxy-4,7,8,9-tetrahydro-1,3-isobenzofurandione

^1H NMR (60 MHz, CDCl_3): δ 0.87 (t, 3H, $J=7.2$ Hz), 2.05 (m, 1H), 2.50 (m, 3H), 3.13 (q, 2H, $J=7.2$ Hz), 3.86 (m, 1H), 5.60 (m, 2H).

^{13}C NMR (CDCl_3): δ 15.08 (q), 21.41 (t), 36.28 (d), 45.78 (d), 64.16 (t), 68.54 (d), 127.03 (d), 131.12 (d), 171.13 (s), 174.34 (s).

Complexation Studies

^1H NMR Determination of the Formation Constants

AN-EBD system. The ^1H NMR chemical shift variations, $\Delta\delta$, between complexed and free states of the 1-ethoxy-1,3-butadiene in this diene-dienophile system were studied in benzene- d_6 solution with tetramethylsilane as internal reference at 25°C and 60°C. The results are given in Tables 14 and 15, respectively.

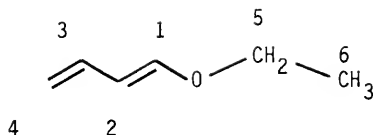


TABLE 14

¹H NMR Data for Determination of Formation Constant of
Complexation of AN-EBD System at 25°C

[EBD] ₀ (mole/l)	[AN] ₀ (mole/l)	H(1)		H(3)		H(5)		H(6)	
		δ obs., (Hz)	Δ (Hz)	δ obs., (Hz)	Δ (Hz)	δ obs., (Hz)	Δ (Hz)	δ obs., (Hz)	Δ (Hz)
0.116	0	642.8	0	608.3	0	334.2	0	93.4	0
0.116	0.975	643.9	1.1	608.3	0	339.7	5.5	96.6	2.8
0.116	2.045	645.3	2.5	608.4	0.1	344.2	10.0	99.2	5.8
0.116	2.949	646.1	3.3	608.3	0	347.4	13.2	101.2	7.8
0.116	4.336	648.6	5.8	608.5	0.2	352.3	18.1	104.0	10.6

TABLE 15

^1H NMR Data for Determination of Formation Constant of
Complexation of AN-EBD System at 60°C

[EBD] ₀ (mole/l)	[AN] ₀ (mole/l)	H(1)		H(3)		H(5)		H(6)	
		δ obs., (Hz)	Δ (Hz)	δ obs., (Hz)	Δ (Hz)	δ obs., (Hz)	Δ (Hz)	δ obs., (Hz)	Δ (Hz)
0.116	0	641.7	0	608.1	0	339.7	0	95.8	0
0.116	0.975	642.7	1.0	607.8	-0.3	344.0	4.3	98.4	2.6
0.116	2.045	643.9	2.2	607.8	-0.3	348.4	8.7	101.0	5.2
0.116	2.949	645.1	3.4	607.9	-0.2	351.8	12.1	103.1	7.3
0.116	4.336	647.0	5.3	-	-	356.0	16.3	105.6	9.8

AN-DABD system. The ^1H NMR chemical shift variations, $\Delta\delta$, between complexed and free states of the 1-diethylamino-1,3-butadiene in this diene-dienophile system were studied in benzene- d_6 solution with tetramethylsilane as internal reference at 25°C. The results are given in Table 16.

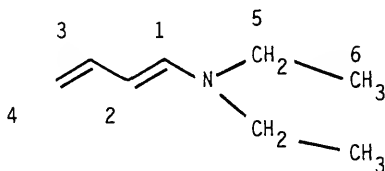


TABLE 16

^1H NMR Data for Determination of Formation Constant of Complexation of AN-DABD System at 25°C

[DABD] ₀ (mole/l)	[AN] ₀ (mole/l)	H(1)		H(5)		H(6)	
		δ obs., (Hz)	Δ (Hz)	δ obs., (Hz)	Δ (Hz)	δ obs., (Hz)	Δ (Hz)
0.086	0	592.3	0	264.4	0	75.4	0
0.086	0.894	594.2	1.9	268.3	3.9	78.2	2.8
0.086	1.806	595.7	3.4	271.7	7.3	80.3	4.9
0.086	2.843	597.4	5.1	275.4	11.0	83.0	7.6
0.086	4.274	600.1	7.8	280.2	15.8	86.2	10.8

^{13}C NMR Chemical Shift Variations

AN-EBD system. The ^{13}C NMR chemical shifts of free and complexed states of 1-ethoxy-1,3-butadiene in AN-EBD system are shown in Table 17.

TABLE 17

^{13}C NMR Data for the Complexed and Uncomplexed EBD Molecules

[EBD] ₀ (mole/l)	[AN] ₀ (mole/l)	C(1)	C(3)	C(4)	C(2)	C(5)	C(6)
		(Hz)	(Hz)	(Hz)	(Hz)	(Hz)	(Hz)
0.116	0	3788.3	3359.8	2783.7	2693.3	1628.8	366.6
0.116	0.975	3789.5	3359.8	2782.4	2693.3	1632.5	366.6
0.116	2.045	3789.5	3359.8	2781.2	2693.3	1633.7	366.6
0.116	2.949	3790.7	3359.8	2781.2	--	1635.0	366.6
0.116	4.336	3789.5	3359.8	2781.2	--	1636.2	--

AN-DABD system. The ^{13}C NMR chemical shifts of free and complexed states of 1-diethylamino-1,3-butadiene in AN-DABD system are shown in Table 18.

TABLE 18

^{13}C NMR Data for the Complexed and Uncomplexed DABD Molecules

$[\text{DABD}]_0$ (mole/l)	$[\text{AN}]_0$ (mole/l)	C(1) (Hz)	C(3) (Hz)	C(4) (Hz)	C(2) (Hz)	C(5) (Hz)	C(6) (Hz)
0.086	0	3539.3	3459.9	2610.3	2499.2	1127.1	326.3
0.086	0.894	3542.9	3461.1	2603.0	2493.1	1127.1	326.4
0.086	1.806	3545.4	3462.4	2598.1	2488.2	1128.4	326.4
0.086	2.843	3546.6	3462.4	2594.4	2484.6	1128.4	326.4
0.086	4.274	3547.8	--	--	2480.9	1128.4	--

Diels-Alder Reactions with Inverse Electron Demand

This author has studied Diels-Alder reactions with inverse electron demand. These reactions were carried out in organic solvents for 2 days with 0.5% by weight of 2,6-Di-*t*-butyl-4-methyl phenol as a free radical inhibitor.

The diene-dienophile pairs of these reactions, reaction conditions and results are shown in Table 19.

TABLE 19
Conditions and Results for Diels-Alder Reactions
with Inverse Electron Demand

Diene ^a	Dienophile ^a	Solvent	Temp. (°C)	Result
DEM	KEA	Toluene	110	No Cycloadduct
DEM	KMA	Toluene	110	No Cycloadduct
DEM	EVE	Ether	25	No Cycloadduct
ESB	KEA	Toluene	110	No Cycloadduct
ESB	KMA	Toluene	110	No Cycloadduct
ESB	EVE	Ether	25	No Cycloadduct
CCB	KEA	Toluene	110	Polymer
CCB	KMA	Toluene	110	Polymer
CCB	DOE	Toluene	110	Polymer
CCB	EVE	Ether	25	Polymer
MPD	KEA	Toluene	110	No Cycloadduct

^aSee Table 1 for footnote description.

CHAPTER III RESULTS AND DISCUSSION

Those polymerizations carried out in benzene solutions may be classified into three categories: 1) the polymerizations of electron-poor dienes with electron-rich dienophiles; 2) the copolymerizations of electron-rich dienes with electron-poor dienophiles; 3) the copolymerizations of electron-rich dienes with electron-poor dienes.

Polymerizations of Electron-Poor Dienes with Electron-Rich Dienophiles

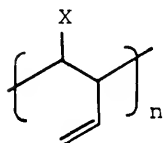
Polymerization of Methyl 2,4-Pentadienoate

The polymerization and copolymerization of methyl 2,4-pentadienoate (MPD) were studied in benzene solution with azobisisobutyronitrile (AIBN) as initiator. The reaction conditions and results are summarized in Tables 1 and 2.

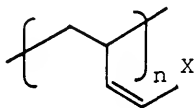
On the basis of the results of elemental analysis and spectral data, the resulting polymers are composed of the diene monomer units only.

The MPD monomer which has two different double bonds, may in principle form polymers of five different types of microstructure, i.e., the 1,2; cis-1,4; trans-1,4; cis-3,4; and trans-3,4 types. The selection of these microstructures should be influenced by the

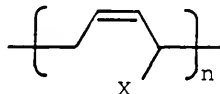
reaction conditions to be adopted and possible geometrical structures of the monomers. The five possible types of microstructure are shown below:



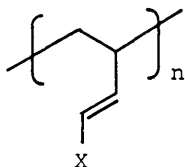
1,2



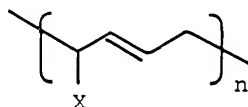
cis-3,4



cis-1,4



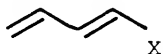
trans-3,4



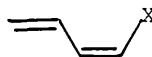
trans-1,4

where $X = \text{CO}_2\text{CH}_3$.

The 1-substituted 1,3-butadiene monomers may consist of two geometrical structures, i.e., the cis-isomer and the trans-isomer.



trans-isomer



cis-isomer

The ^1H NMR and ^{13}C NMR spectra of MPD monomer are shown in Figures 6 and 7, respectively. Because of the steric factor, the olefinic carbons of these geometrical isomers should appear at different chemical shifts in the ^{13}C spectra. But in Figure 7, there are only four peaks corresponding to the olefinic carbons. In the infrared spectrum, an absorption was seen at 961 cm^{-1} which is characteristic of the trans-1,4 structure. Therefore, the MPD monomer synthesized was proven to have the trans geometrical structure only.

Microstructure of Poly(Methyl 2,4-Pentadienoate)

Infrared spectroscopy is very useful to distinguish the microstructure of diene polymers. The most characteristic vibrational modes of olefins are out-of-plane C-H bending vibrations between 1000 and 650 cm^{-1} . In the infrared spectra of the resulting polymers, absorptions were seen at 722 , 910 and 968 cm^{-1} which are characteristic of cis-1,4, trans-3,4 and trans-1,4 structures, individually.

The ^1H NMR and ^{13}C NMR spectra of the resulting polymers are shown in Figures 8 and 9, respectively. In Figure 8, the peaks at δ 5.43 and 5.50 are assigned to the olefinic protons of the trans-1,4 structure and the peaks at δ 5.87 and 6.60 are assigned to those of the trans-3,4 structure. A broad peak at δ 2.33 is attributable to the methylene protons. The broad peak at δ 3.00 is attributable to the methine proton, and a peak at δ 3.64 is attributable to the protons of methyl group. The integration of ^1H NMR spectrum shows

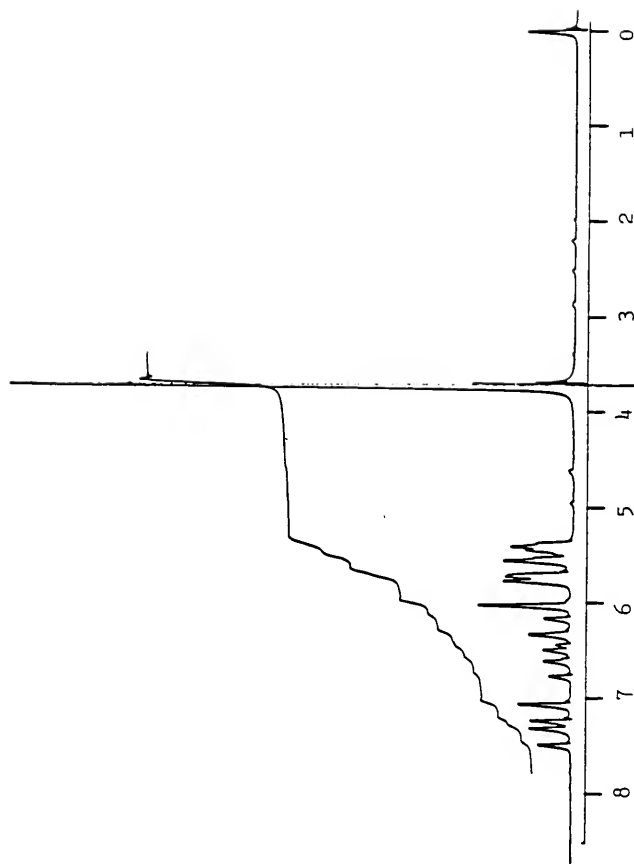


Figure 6. ^1H NMR (60 MHz) Spectrum of Methyl 2,4-Pentadienoate in CDCl_3 at 25°C .

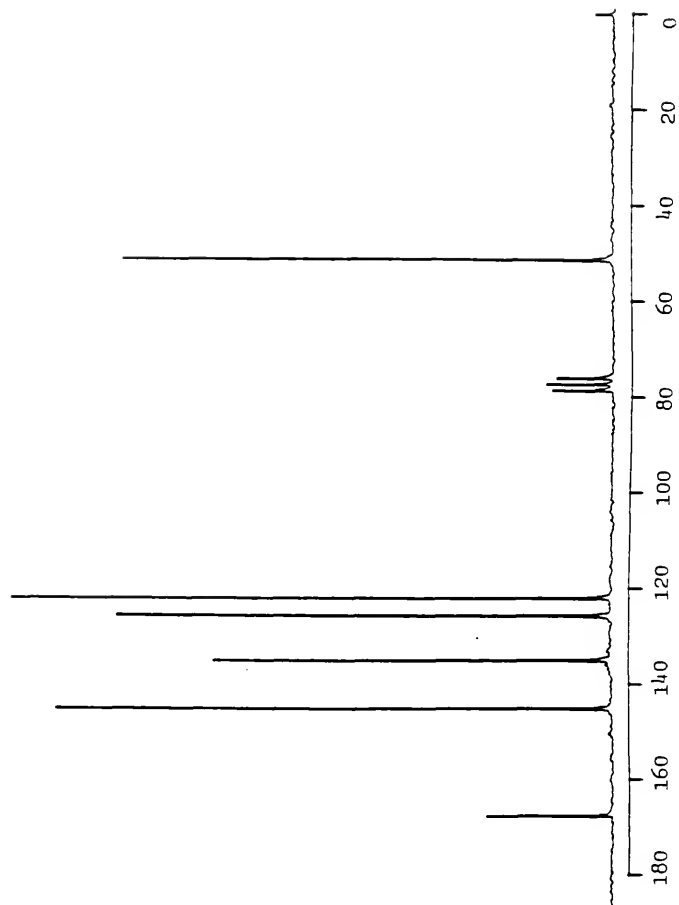


Figure 7. ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of Methyl 2,4-Pentadienoate in CDCl_3 at 25°C .

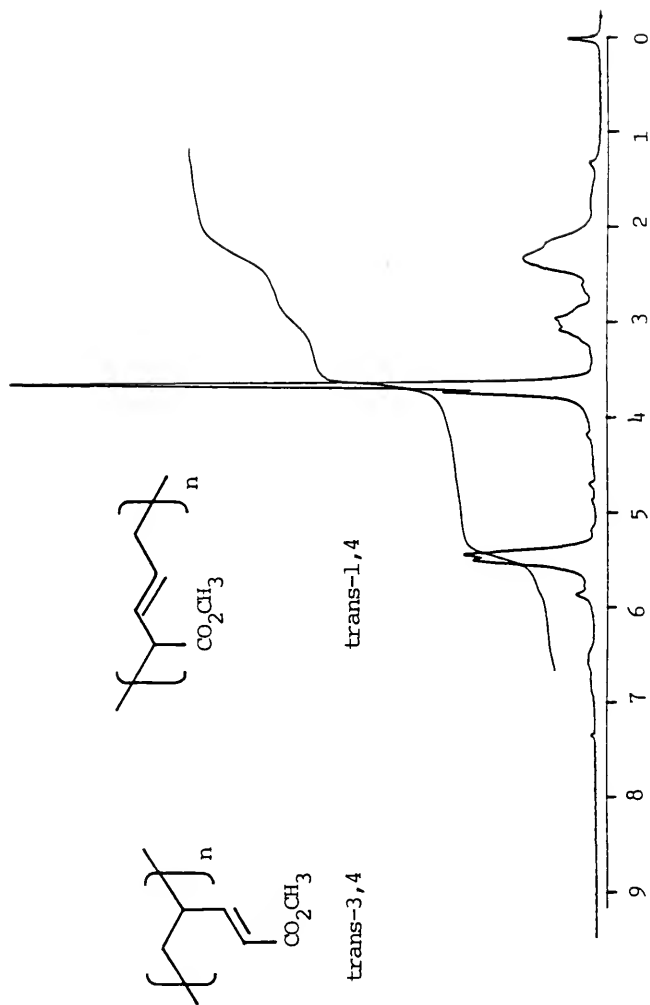


Figure 8. ^1H NMR (60 MHz) Spectrum of Poly(Methyl 2,4-Pentadienoate) in CDCl_3 at 25°C .

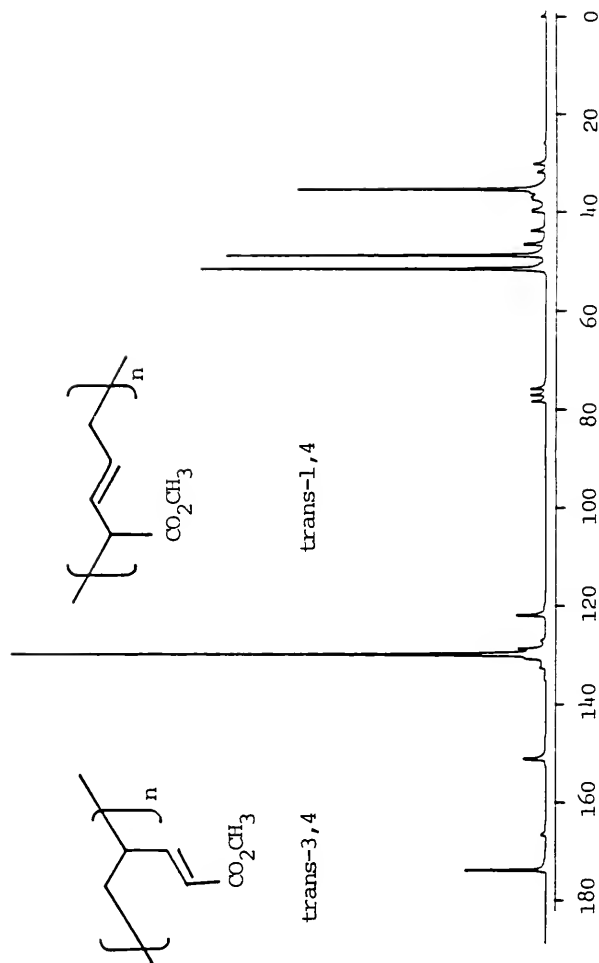


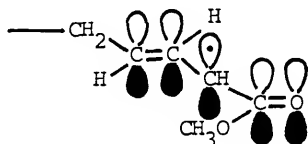
Figure 9. ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of Poly(Methyl 2,4-Pentadienoate) in CDCl_3 at 25°C .

that the polymers consist of 90% of trans-1,4 and cis-1,4 structures and 10% of trans-3,4 structure.

In Figure 9, the peaks at δ 173.45 and 166.29 are assigned to the carbonyl carbons of the trans-1,4 and the trans-3,4 structures, individually. The peaks at δ 150.74 and 121.64 are assigned to the olefinic carbons of the trans-3,4 structure, the peaks at δ 132.32 and 129.39 are assigned to those of the trans-1,4 structure. The peak at δ 51.46 is attributable to the carbon of the methyl group ($-\text{CO}_2\text{CH}_3$) of the trans-1,4 structure. The peaks at δ 48.73 and 35.23 are assigned to the methine carbon and methylene carbon, respectively, of the trans-1,4 structure.

On the basis of all spectral results, poly(methyl 2,4-pentadienoate) obtained with radical initiation was mainly composed of trans-1,4 units.

The trans-positioned electron clouds of the propagating radical, conjugated with the allyl group and the carbonyl group in the same plane seems to be most stable; this could be the reason why trans-1,4 units constitute the main structure of the polymers.



The MPD is a monomer which was readily polymerized with the use of the radical initiator. In some cases, the electron donor-acceptor complex can be activated thermally or photochemically to generate the free radical necessary for initiation of polymerization. In the copolymerization of MPD and n-butyl vinyl ether without free radical initiator added, there was no polymer isolated. This result shows the donor-acceptor interaction of this monomer pair is probably too weak to form a reactive intermediate of free radical nature.

Polymerization of 1-Carbethoxy-1-cyano-1,3-butadiene

The polymerization and copolymerization of 1-carbethoxy-1-cyano-1,3-butadiene (CCB) were carried out in benzene solution with and without AIBN as initiator. The reaction conditions and results are summarized in Tables 3 and 4.

On the basis of the results of elemental analysis and spectral data, the resulting polymers are composed of the diene monomer units only.

The chemical properties of CCB are very similar to ethyl α -cyanoacrylate which is the important component in "super glue." These monomers have two strong electron-withdrawing groups on one olefinic carbon, so they are polymerized very easily by anionic initiation. Therefore, to this polymerization system, about 1% by weight of benzoic acid was added as anionic inhibitor.

Microstructure of Poly(1-Carbethoxy-1-cyano-1,3-butadiene)

In the region of C-H out-of-plane vibration in the infrared spectra of the resulting polymers, a strong absorption band at 970 cm^{-1} ascribable to the trans-1,4 structure was observed.

The ^1H NMR and ^{13}C NMR spectra of the resulting polymers are shown in Figures 10 and 11, individually. In Figure 10, the peaks at δ 5.66 and 5.88 are assigned to the olefinic protons. The peaks centered at δ 4.30 correspond to methylene protons ($-\text{CO}_2\text{CH}_2-$), and the peaks centered at δ 1.32 correspond to the protons of methyl group. A broad peak at δ 2.78 is assigned to the methylene protons of the polymer backbone.

In Figure 11, the peak at δ 166.09 is assigned to the carbonyl carbon. The peaks at δ 130.37 and 127.25 are assigned to the olefinic carbons. The peak at δ 116.23 corresponds to the nitrile carbon. The peaks at δ 63.60 and 39.75 are assigned to the methylene carbon ($-\text{CO}_2\text{CH}_2-$) and the methylene carbon ($-\text{CH}_2-\text{CH}=\text{CH}-$), individually. The peak at δ 51.66 is assigned to the quaternary carbon on the polymer backbone. One peak at δ 13.89 corresponds to the carbon of the methyl group. Based on the spectral data, it was found that poly(1-carbethoxy-1-cyano-1,3-butadiene) is composed of the trans-1,4 microstructure only. This result can be rationalized by the same explanation given for poly(methyl 2,4-pentadienoate), i.e., the trans-positioned electron clouds of the propagating radical, conjugated with the allyl group, the carbonyl group and the nitrile group in the same plane seems to be most stable.

The CCB is a monomer which is readily polymerized by free radical or anionic initiation. In Tables 3 and 4, sample 13 shows that with benzoic acid as anionic inhibitor, CCB could not be polymerized thermally in benzene solution without free radical initiation. Sample 14 shows that with benzoic acid as anionic inhibitor,

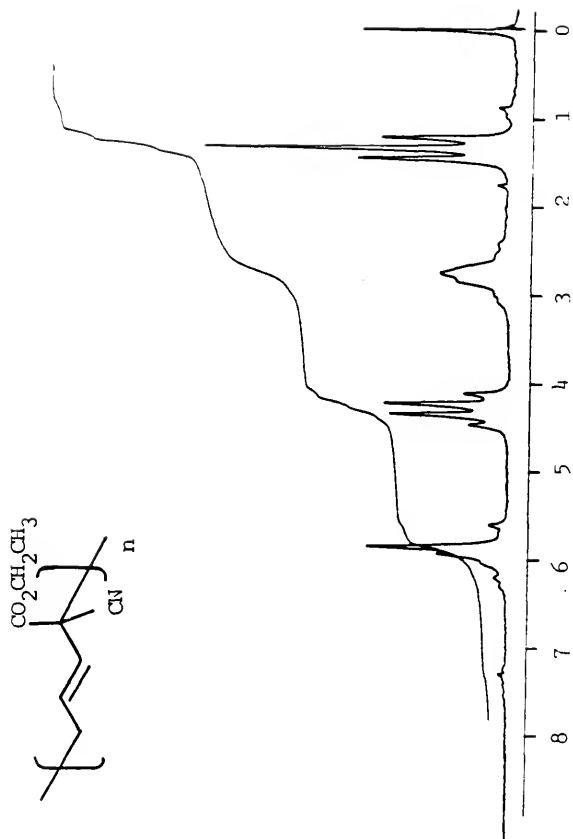


Figure 10. ^1H NMR (60 MHz) Spectrum of Poly(1-Carbethoxy-1-cyano-1,3-butadiene) in CDCl_3 at 25°C .

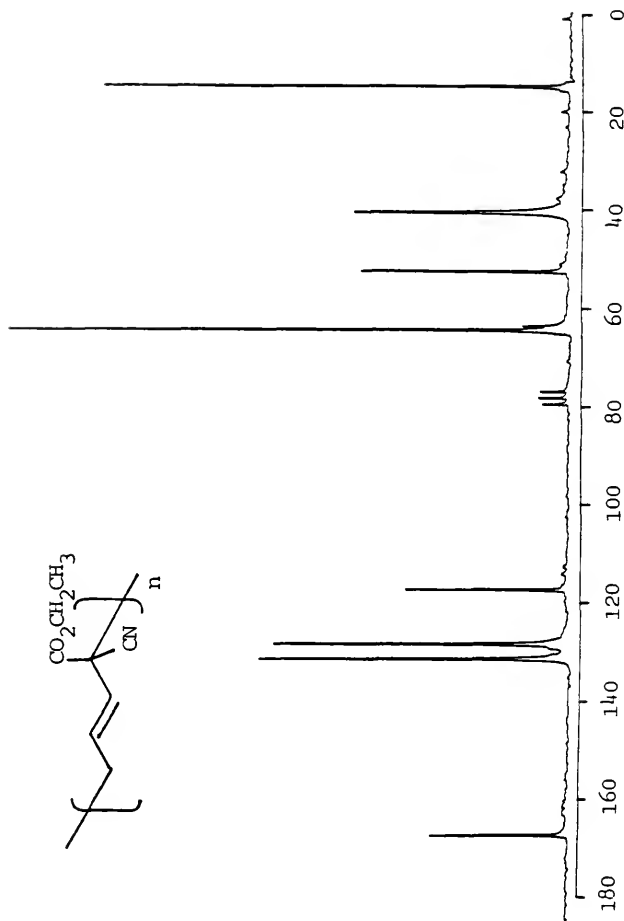


Figure 11. ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of Poly(1-Carboxy-1-cyano-1,3-butadiene) in CDCl_3 at 25°C .

CCB could be polymerized in benzene solution with free radical initiation. Sample 8 shows that spontaneous polymerization of a 1:1 monomer feed ratio of CCB and n-butyl vinyl ether (BVE) produced a high yield of poly(CCB). Sample 9 shows that when polymerization under similar conditions to sample 8, except that a large amount of benzoic acid was added, the yield of poly(CCB) was much lower than that of sample 8. Sample 10 shows that when polymerization under similar conditions to sample 8 except that only a small amount of benzoic acid was added, the yield of poly(CCB) was similar to that of sample 8. Sample 11 shows that under similar polymerization conditions to sample 8, except a large amount of radical inhibitor was added, the yield of poly(CCB) was zero.

On the basis of these investigations, the interaction of CCB with electron-rich dienophiles probably forms a reactive intermediate of free radical nature to initiate polymerization.

Polymerization of 1-Cyano-1,3-butadiene

The polymerization and copolymerization of 1-cyano-1,3-butadiene (CBD) were studied in benzene solution with AIBN as initiator. The reaction conditions and results are shown in Tables 9 and 10.

The mixture of cis and trans CBD isomers was used for these polymerizations. On the basis of spectral data, the resulting polymers were composed of the diene monomer units exclusively.

In the infrared spectra of the resulting polymers, two absorption bands in the nitrile group stretching region were observed: an absorption at 2238 cm^{-1} which may be due to the nitrile group attached to a saturated carbon atom, and one at 2220 cm^{-1}

possible originated by a nitrile group attached to an unsaturated carbon atom.

Mechanism of Polymerization of Electron-Poor Dienes and Electron-Rich Dienophiles

Frontier orbital theory has successfully explained many free radical reactions. For a radical, the frontier orbital is the singlet occupied molecular orbital (SOMO). This orbital interacts with both the HOMO and LUMO of the closed shell substrates and the perturbation energy is in inverse ratio to the energy difference between frontier orbitals.

Radicals with a higher energy SOMO (nucleophilic radicals) should react fast with substrates with a low energy LUMO, and radicals with lower energy SOMO (electrophilic radicals) should react fast with substrates with a high energy HOMO. Figure 12⁴⁶ shows the frontier orbital energies and coefficients for 1-substituted dienophile donors and 1-substituted diene acceptors.

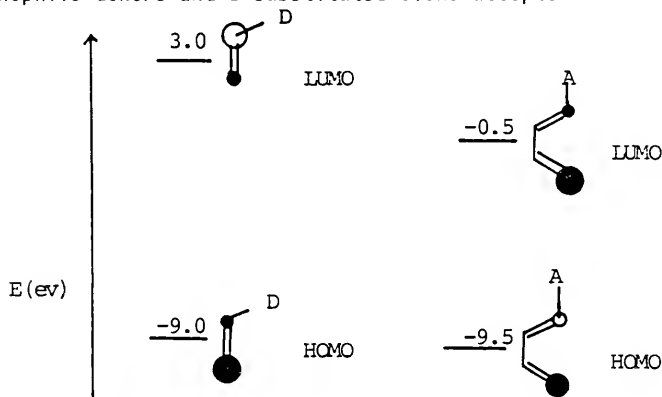


Figure 12. Frontier Orbital Energies and Coefficients for 1-Substituted Dienophile Donors and 1-Substituted Diene Acceptors.

The SOMO-LUMO interaction is always stabilizing, but the SOMO-HOMO interaction (two orbitals, three electrons) is not always stabilizing. Bernardi et al.⁴⁷ have shown this phenomena by inclusion of overlap in the theoretical analysis. Their method may lead to a better understanding of the nature of the two orbitals-three electrons interaction.

For the polymerization system of electron-poor dienes and electron-rich dienophiles, the difference of HOMO energies between diene and dienophile is only 0.5 eV (shown in Fig. 12). So the SOMO-HOMO interaction may not be a decisive factor to these reactions. On the other hand, the difference of LUMO energies between them is 3.5 eV, and also this interaction is always stabilizing. The interaction of SOMO-LUMO should play a more significant role than that of SOMO-HOMO.

Not only the energies of the frontier orbitals but also the coefficients of the corresponding atomic orbitals are of importance in the interaction. In Figure 12, for 1-substituted electron-rich dienophile, the substituted LUMO coefficient is larger than the unsubstituted LUMO coefficient. With the consideration of orbital overlap factor, a free radical would attack at the substituted position of this type monomer. However, another factor, the steric α -effect, should destabilize this interaction. For a 1-substituted electron-poor diene, the unsubstituted LUMO coefficient is larger, and free radical attack at this position would not cause steric repulsion. Based on these factors, we can successfully explain why the resulting polymers are composed of diene monomer only.

Copolymerizations of Electron-Rich Dienes with Electron-Poor Dienophiles

Copolymerization of 1-Ethoxy-1,3-butadiene and Acrylonitrile

The copolymerizations of 1-ethoxy-1,3-butadiene (EBD) with acrylonitrile (AN) were carried out by free radical or spontaneous initiation in benzene at 60°. In addition to the resulting copolymers, an appreciable amount of Diels-Alder adducts were formed as by-product. The reaction conditions and results are shown in Tables 5, 6, 9 and 10.

A structural study of AN-EBD copolymer was undertaken to confirm its alternating nature and to determine its microstructure.

Monomer Reactivity Ratio of EBD and AN

In order to determine the monomer reactivity ratios of EBD and AN, the copolymerizations were performed by radical initiation with various monomer feed ratios in benzene at 60°, where the concentrations of the total monomer and free radical initiator (AIBN) were kept constant at 5.5 M and 1.3×10^{-2} M, respectively.

The compositions of the resulting copolymers with low conversion (about 10%) were determined by elemental analysis. The results and conditions are shown in Table 12. It was found that the copolymers have a highly alternating structure, even with varying feed ratios of monomers, as judged on the basis of nitrogen analysis and NMR measurement.

Figure 13 shows the EBD content of copolymers obtained in the presence of the AIBN initiator system gives an almost constant value of 49-57% irrespective of a wide range of variations of monomer feed ratios.

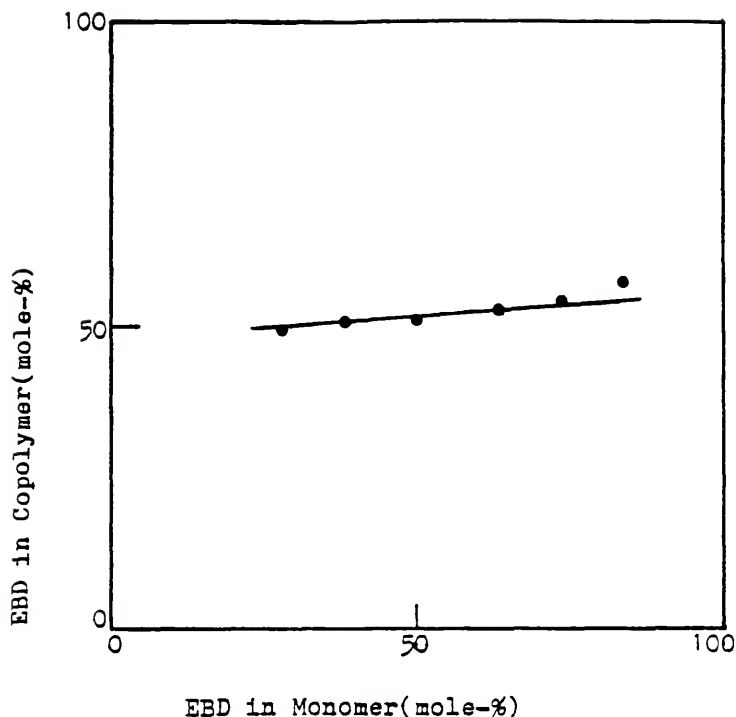


Figure 13. Monomer Feed--Copolymer Composition Curve for Copolymerization System of EBD and AN.

The ^1H NMR and ^{13}C NMR spectra of the resulting copolymers are shown in Figures 14 and 15.

According to the copolymer composition equation, many methods have been developed since 1944 to determine the monomer reactivity ratios r_1 and r_2 . The most accurate method may be the nonlinear least-square method that was developed by Tidwell and Mortimer.⁴⁸ However, this method is most tedious because of the computer

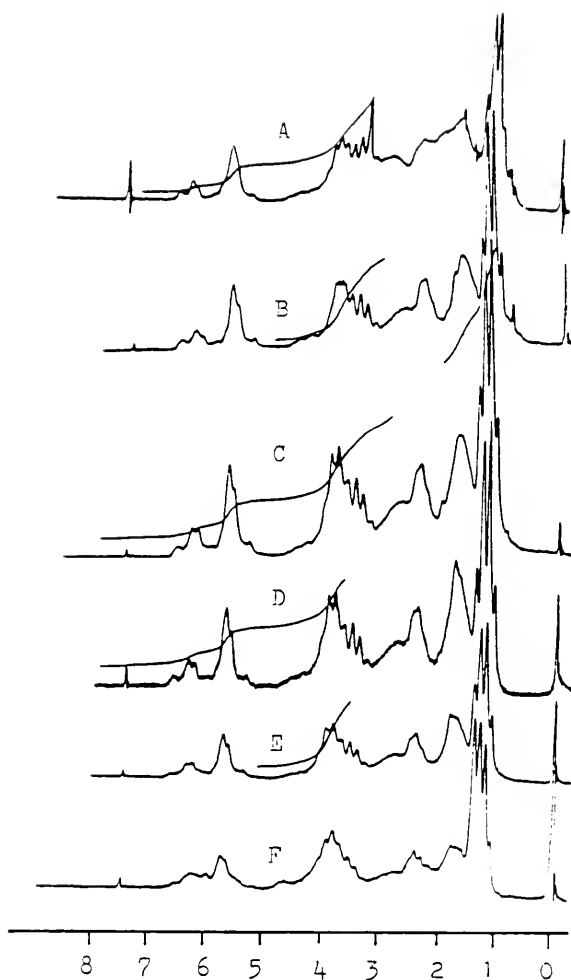


Figure 14. ^1H NMR Spectra of AN-EBD Copolymers, Except D (Spontaneous Initiation), the Others Prepared with Free Radical Catalysts. Copolymer Compositions of EBD(%): (A) 14.9; (B) 49.6; (C) 50.6; (D) 52.3; (E) 54.0; (F) 57.5.

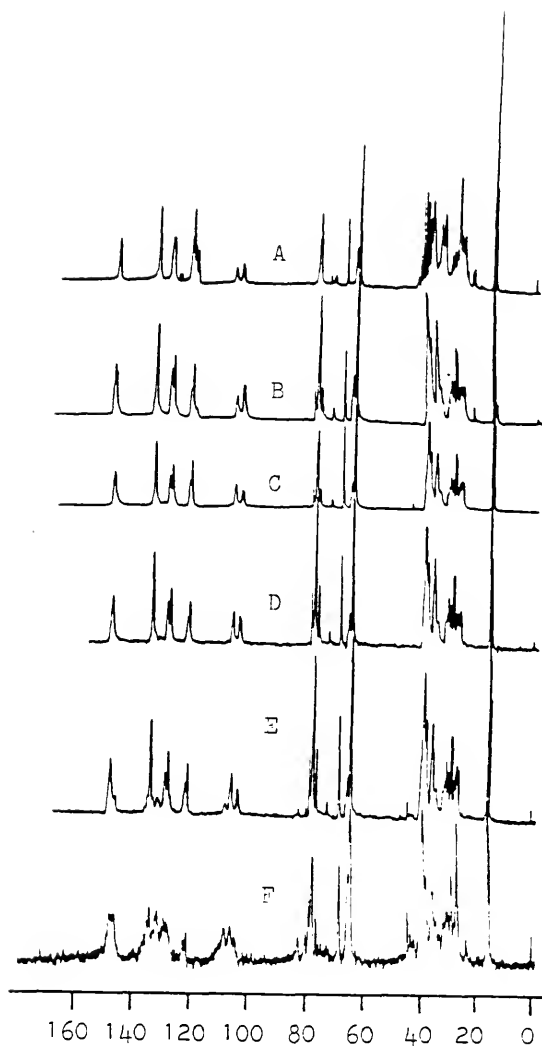


Figure 15. ^1H Decoupled ^{13}C NMR Spectra of AN-EBD Copolymers, Except D (Spontaneous Initiation), the Others Prepared with Free Radical Catalysts. Copolymer Compositions of EBD(%): (A) 14.9; (B) 49.6; (C) 50.6; (D) 52.3; (E) 54.0; (F) 57.5.

iteration that is required. For this work, the monomer reactivity ratios r_1 and r_2 were determined by Fineman-Ross method⁴⁹ and Kelen-Tudos method,⁵⁰ individually.

Fineman-Ross equation:

$$\frac{(1/F_1 - 2)}{(1/f_1 - 1)} = r_2 - r_1 \frac{(1/F_1 - 1)}{(1/f_1 - 1)^2} \quad (14)$$

where F_1 = mole fraction of monomer 1 in copolymer,

f_1 = mole fraction of monomer 1 in feed.

Figure 16 shows the plot according to the Fineman-Ross equation.

Kelen-Tudos equation:

$$\frac{G}{\alpha + F} = (r_1 + \frac{r_2}{\alpha}) \frac{F}{\alpha + F} - \frac{r_2}{\alpha} \quad (15)$$

where $G = x(1 - 1/y)$; $x = [M_1]/[M_2]$ in monomer feed; $F = x^2/y$; and $y = d[M_1]/d[M_2]$ in the copolymer; α is an arbitrary constant,

preferably equal to $(F_M F_m)^{0.5}$, F_M and F_m being the highest and the lowest values of F ; (1 and 2 represent the monomers EBD and AN). The plot according to the Kelen-Tudos equation is shown in Figure 17.

The monomer reactivity ratios r_1 and r_2 , were calculated by both methods, then the Alfrey-Price Q and e values were calculated from them. The results are summarized in Table 20.

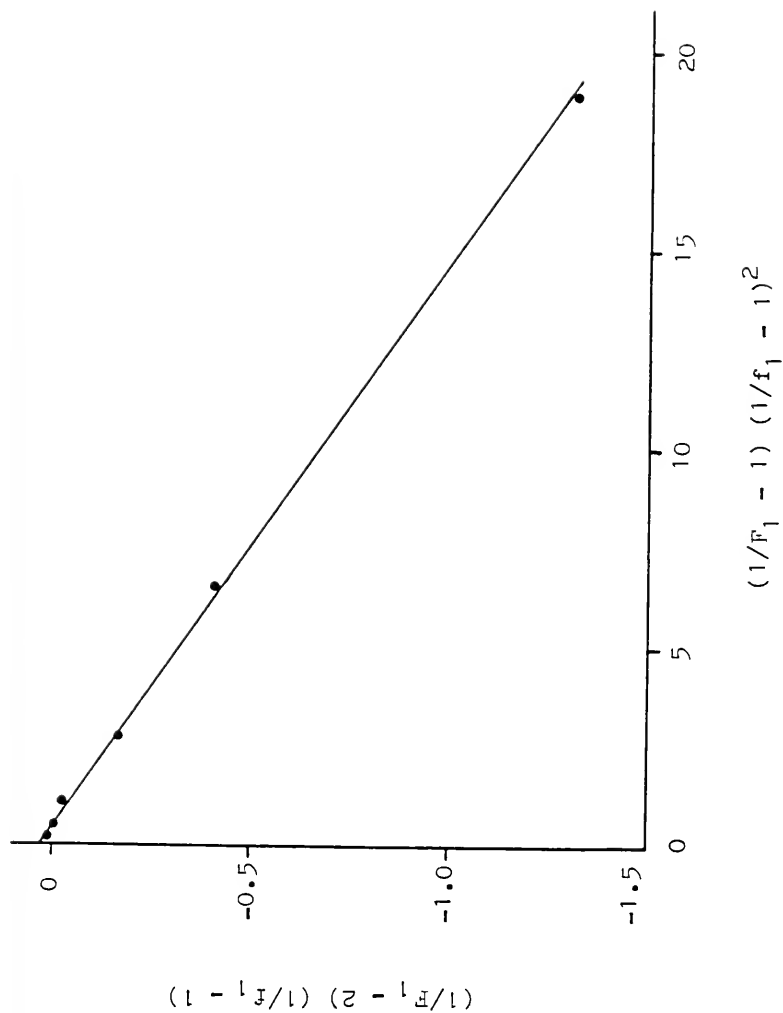


Figure 16. Plot According to the Method of Fineman-Ross for the AN-EBD Copolymer System.

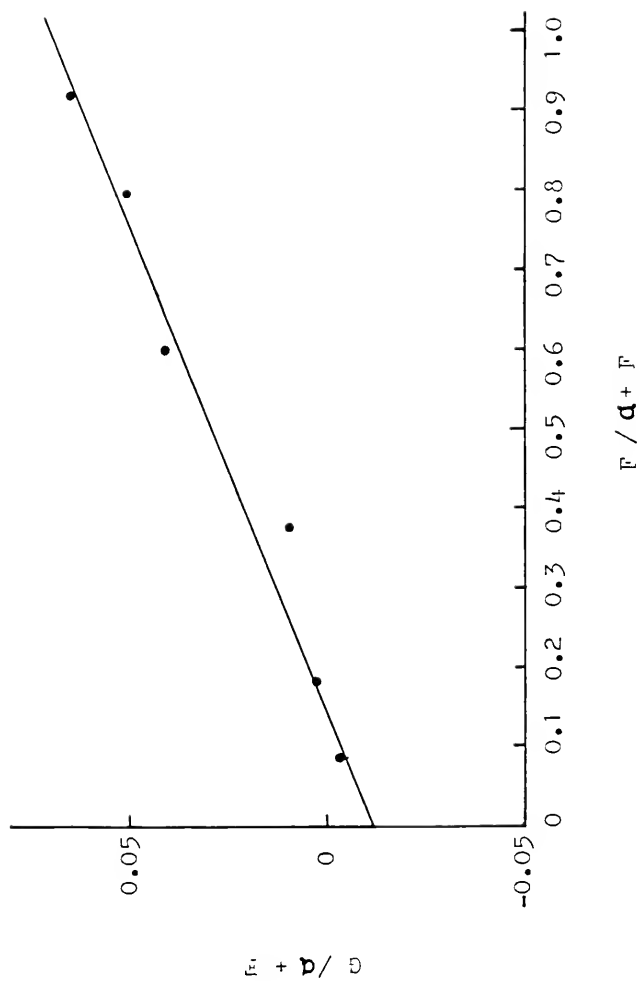


Figure 17. Plot According to the Method of Kelen-Tudos for the AN-EBU Copolymer System.

TABLE 20

Monomer Reactivity Ratios and Alfrey-Price Q and e Values
for the Free Radical Initiated Copolymerization of EBD and AN

Calculation Method	r_1	r_2	e	Q
Fineman-Ross	0.071	0.029	-1.287	1.046
Kelen-Tudos	0.069	0.022	-1.348	1.284

Judging from the fact that the product of the monomer reactivity ratios is close to zero, the copolymer should have a high degree of alternation of EBD and AN units in the chain.

Microstructure of AN-EBD Copolymers

In the infrared spectra of AN-EBD copolymers, absorptions were seen at 729, 754, 938 and 972 cm^{-1} which are characteristic of cis-3,4, cis-1,4, trans-3,4 and trans-1,4 structures, respectively.

The ^1H NMR spectrum of 1:1 molar ratio AN-EBD copolymer is shown in Figure 18. On the basis of integration of olefinic protons, the copolymers are composed of 51% trans and cis-1,4 addition and 49% trans and cis-3,4 addition. Table 21 shows the assignments of chemical shifts in ^1H NMR spectrum of AN-EBD copolymer, based on two polymer sequence units I and II.

The ^1H decoupled ^{13}C NMR spectrum of 1:1 molar ratio AN-EBD copolymer is shown in Figure 19. Along with off-resonance and INEPT spectra, the assignments of chemical shifts in Figure 19 are shown in Table 22, based on polymer sequence units I and II.

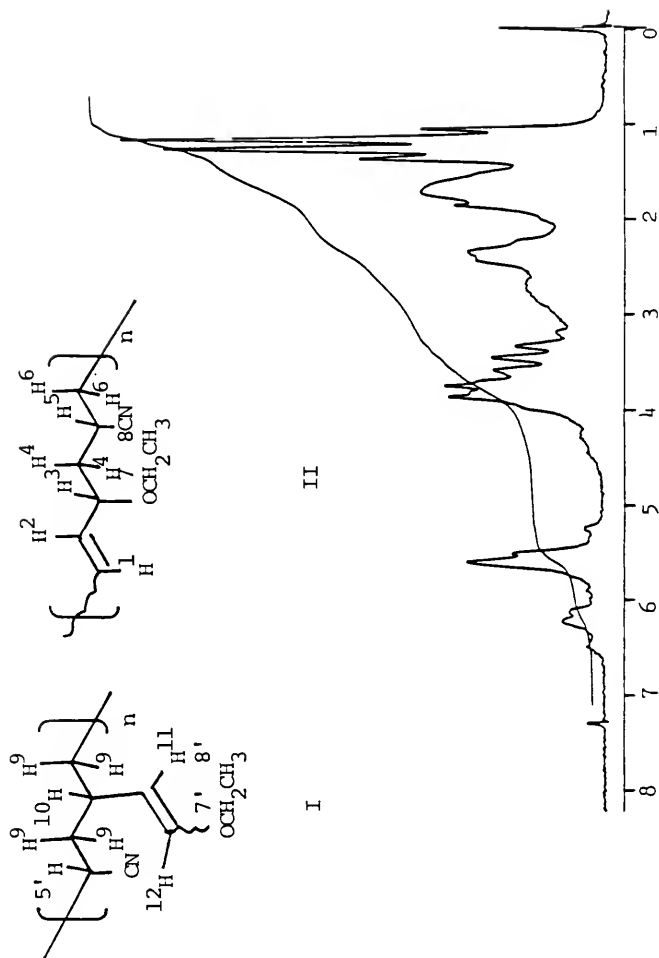


Figure 18. ^1H NMR (60 MHz) Spectrum of AN-EBD Copolymer in CDCl_3 at 25°C .

TABLE 21

Assignments of Chemical Shifts in ^1H NMR Spectrum
of AN-EBD Copolymer

Proton Assignments	Chemical Shifts δ (observed)	Chemical Shifts δ (calculated) ⁵²	Number of Protons
12	6.20	6.20	0.5
1, 2	5.53	5.46	1.0
11	4.27	4.66	0.5
3, 7, 7'	3.13-4.03	3.55, 3.75	2.5
5, 5'	2.70	2.60	1.0
6, 10	2.36	2.39	1.5
4, 9	1.43-2.06	1.61, 1.76	3.0
8, 8'	1.23	1.22	3.0

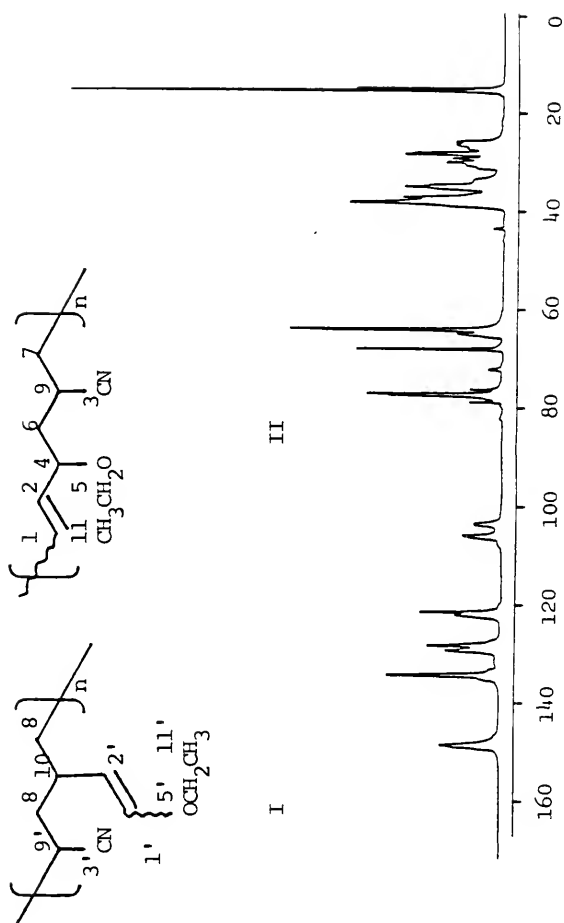


Figure 19. ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of AN-EBD Copolymer in CDCl_3 at 25°C .

TABLE 22

Assignments of Chemical Shifts in ^{13}C NMR Spectrum
of AN-EBD Copolymer

Carbon Assignments	Chemical Shifts δ (observed)	Chemical Shifts δ (calculated) ⁵¹⁻⁵³
1'	148.06	144, 142.9
1, 2	133.88, 128.76, 127.78	133.6, 132.5, 130.6, 129.5
3, 3'	121.69, 121.01	
2'	105.46, 103.22	106.5, 105.4
4	76.61, 71.59	80.9, 75.6
5, 5'	67.59, 64.43, 63.70	
6	37.77, 36.70	36.1
7, 8	34.55	34.1, 33.0
9'	30.75, 29.53, 28.70	30.0
9	27.87, 27.58	26.1
10	26.17, 25.87, 25.34	24.0
11, 11'	14.86, 14.78	

Determination of Formation Constant of Charge-Transfer Complex

The formation constant (K_f) of the charge-transfer complex (C) between a donor (D) and an acceptor (A) is characterized as follows:



$$K_f = \frac{[C]}{[D][A]} \quad (17)$$

Evidence for the formation of a weak charge-transfer complex is the appearance of a new absorption band in the ultraviolet-visible region of the spectrum and occasional appearance of color on mixing the two components. However, in some cases, a new band fails to be distinguished in the electronic spectrum because of overlap of the absorptions of the donor and/or acceptor. Other techniques must be used to identify the presence of a complex. For example, proton chemical shifts in the NMR spectra may provide evidence for complex formation in many cases.

In order to study complex participation in copolymerization, it is necessary to establish that a molecular complex is formed between the monomers. The UV and NMR methods were utilized to study the formation constant of charge-transfer complex in the AN-EBD system. The UV method was performed in n-hexane solution at room temperature, but no charge-transfer bands could be detected spectrophotometrically.

The formation constants of AN-EBD system were determined by the NMR method using the equation that was developed by Foster and Fyfe.⁵⁴

$$\frac{\Delta}{[A]_0} = -\Delta K_f + \Delta_0 K_f \quad (18)$$

where $\Delta = \delta_{\text{obsd}}^D - \delta_O^D$ is the difference between the chemical shift of the donor protons in complexing media (δ_{obsd}^D) and the shift of the donor in uncomplexed form (δ_O^D), $\Delta_0 = \delta_{AD}^D - \delta_O^D$ is the shift for the pure complex relative to the shift for the pure donor, $[A]_0$ is the concentration of the acceptor, in this case, the concentration of acceptor in large excess so that the experimental data can be utilized in a linear plot according to equation 18. The proton chemical shifts of EBD were measured with various concentrations of AN in benzene- d_6 solution. Tables 14 and 15 summarize the results that were measured at 25° and 60°, respectively.

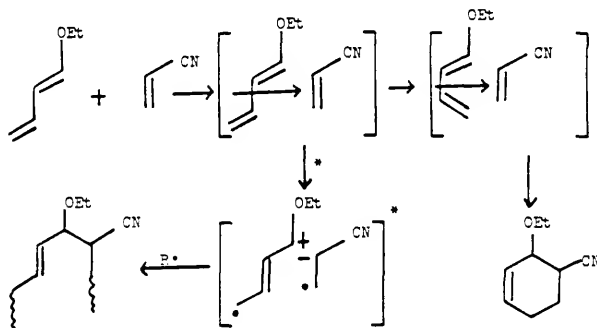
By plotting $\Delta/[A]_0$ vs Δ , straight lines were obtained, the slope and intersection with the ordinate permit the calculation of the formation constant. Based on the chemical shifts of methylene protons ($-OCH_2-$), the values of K_f calculated are 0.12 at 25° and 0.05 at 60°. However, it was found that the chemical shift of the TMS peak was affected by the composition of the mixture, so the spectra were calibrated via a characteristic signal of the deuterated benzene. Based on these corrected chemical shift values, the values of K_f calculated are 0.19 at 25° and 0.10 at 60°. Due to the complex formation, the chemical shifts of the protons in the EBD monomer

moved to lower magnetic field in ^1H NMR spectra. These shifts reflected the decreasing electron density on the protons of the EBD monomer on the complex formation. It is apparent that the formation constant is increased by lowering the temperature.

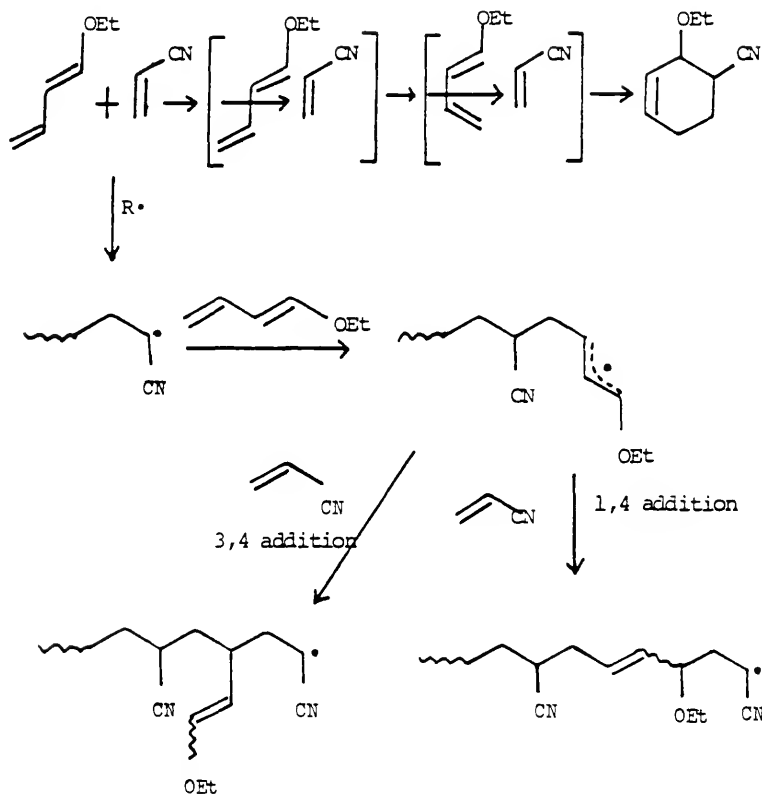
The ^{13}C NMR spectra may reveal the p-electron density of the carbons in the EBD monomer. The carbon chemical shifts of EBD were measured with various concentrations of AN in benzene- d_6 solution at 25° . The results are summarized in Table 16. The formation of 1:1 complex caused downfield shifts of methylene carbon ($-\text{OCH}_2-$), but hardly shifted the olefinic carbons at all. The EBD in the AN-EBD system may be related to the so-called "n-type" donor, i.e., the lone pair electrons of the donor transfer to the acceptor in the complex formation.

Mechanistic Study of AN-EBD Alternating Copolymer

It was proposed that alternating copolymers may result from homopolymerization of charge-transfer complexes generated by the interaction of electron donor monomers with electron acceptor monomers. According to this postulation, the reaction scheme for AN-EBD system is shown as follows:

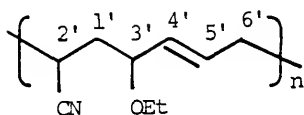


Another reaction scheme in accordance with the free monomer mechanism is shown below:

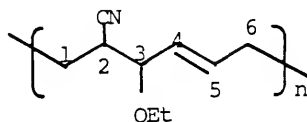


There are two possible polymer sequence structures for the trans-1,4 addition in the repeating unit of the alternating

copolymer. Structure I would be formed via the free monomer mechanism, and the structure II would be formed via the complex mechanism.



Structure I (head-to-tail)



Structure II (head-to-head)

Both ^1H NMR and ^{13}C NMR spectra may provide evidence in favor of one of these two structures. To clarify this point, the proton chemical shifts of both sequence structures were calculated. Judging from the chemical shifts and integrations, structure I was shown to be the preferred sequence unit in the alternating copolymer. On the contrary, if structure II had been the real sequence unit, in the chemical shift range δ 1.43-2.06 integration should have shown four protons instead of three protons actually observed in the spectrum.

Based on the carbon chemical shifts calculated, a peak of the methine carbon (2) should appear at δ 36.1 and a peak of the methylene carbon (1) should appear at δ 30.0 for structure II. However, the spectrum obtained by INEPT technique showed that there was no methylene carbon peak in the range of δ 24-32, and no methine carbon peak in the range of δ 34-40 either. Therefore, the evidence favors structure I as the real sequence unit in the alternating

copolymer, and the propagation step via the free monomer mechanism probably predominates under the polymerization conditions employed.

It was found that the AN-EBD alternating copolymer could be formed without free radical catalyst. But no copolymer could be prepared in the presence of a radical inhibitor. So the interaction of donor-acceptor in this system probably forms a reactive intermediate of free radical nature to initiate polymerization.

The relative reactivity of this comonomer pair in radical alternating copolymerization is discussed qualitatively in terms of frontier orbitals.

It should be expected that the donor-acceptor interaction between the growing radicals and monomers would significantly reduce their activation energies for transition state formation. Radicals with a higher energy SOMO will react fast with a substrate with a low energy LUMO, and radicals with a lower energy SOMO will react fast with a substrate with a high energy HOMO.

These considerations may successfully explain the alternating character of the radical AN-EBD copolymerization. The growing radical EBD \cdot is adjacent to an oxygen atom, thus this radical has a high energy SOMO. It reacts faster with a molecule (AN) with a lower energy LUMO. On the other hand, the growing radical AN \cdot is adjacent to a nitrile group which acts as an electron-withdrawing substituent; thus this radical has a low energy SOMO, and it reacts faster with a molecule (EBD) with a higher energy HOMO.

Figure 20 shows the frontier orbital energies and coefficients for 1-substituted dienophile acceptors and 1-substituted diene donors.⁴⁶

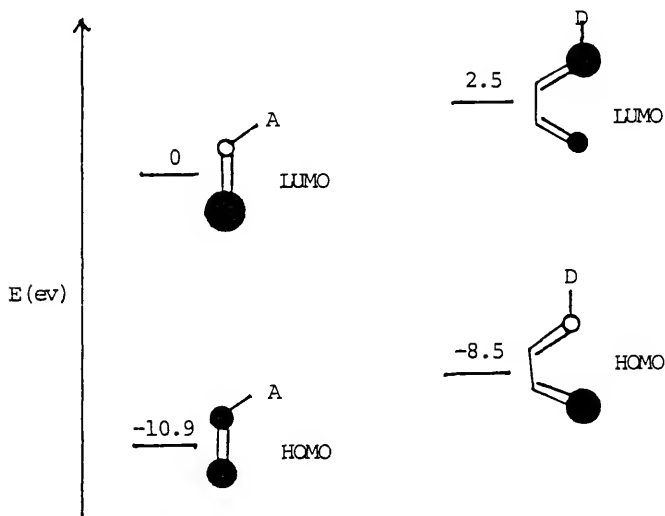


Figure 20. Frontier Orbital Energies and Coefficients for 1-Substituted Dienophile Acceptors and 1-Substituted Diene Donors.

According to the carbon chemical shifts in the ^{13}C NMR spectra of EBD, electron densities of C2 and C4 are larger than those of C1 and C3. In addition to the steric factor, the growing radical AN^\bullet should attack at C4 of molecule EBD. This explanation is in good

agreement with the structure of the resulting copolymer which consists of trans-1,4, cis-1,4, trans-3,4 and cis-3,4 structures.

Copolymerization of 1-Diethylamino-1,3-butadiene and Acrylonitrile

The copolymerization of 1-diethylamino-1,3-butadiene (DABD) with acrylonitrile (AN) were carried out by free radical initiation in benzene at 60°. In addition to the resulting copolymers, an appreciable amount of Diels-Alder adducts were formed as by-product. The reactions conditions and results are shown in Tables 5 and 6.

A structure study of AN-DABD copolymer was undertaken to confirm its alternating nature and to determine its microstructure.

Monomer Reactivity Ratio of DABD and AN

To determine the monomer reactivity ratio of DABD and AN, radical copolymerizations initiated by AIBN were carried out in benzene at 60° with various monomer feed ratios, where the concentrations of total monomer and AIBN were kept constant at 5.8 M and 1.4×10^{-2} M, respectively. The results and conditions are shown in Table 13. It was found that the copolymer has a highly alternating structure, even with varying feed ratios of monomer, as judged on the basis of elemental analysis results.

The monomer reactivity ratios r_1 and r_2 of the comonomer pair were determined by Fineman-Ross method and Kelen-Tudos method, respectively. The plot according to the Fineman-Ross method is shown in Figure 21, and the plot according to the Kelen-Tudos method is shown in Figure 22. The monomer reactivity ratios r_1 and r_2 were calculated by both methods. The results are summarized in Table 23.

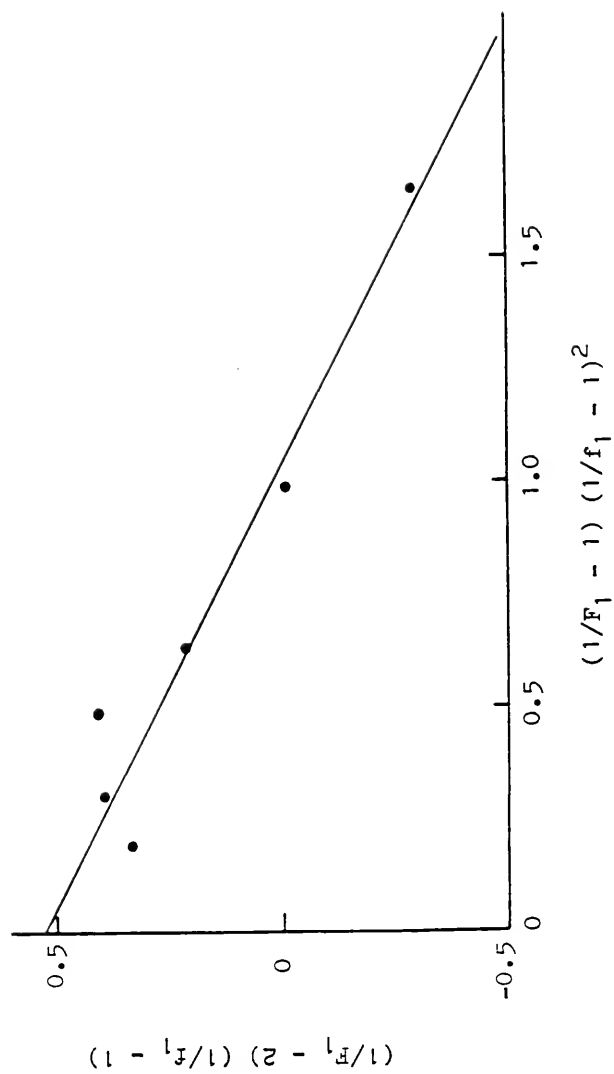


Figure 21. Plot According to the Method of Fineman-Ross for the AN-DABD Copolymer System.

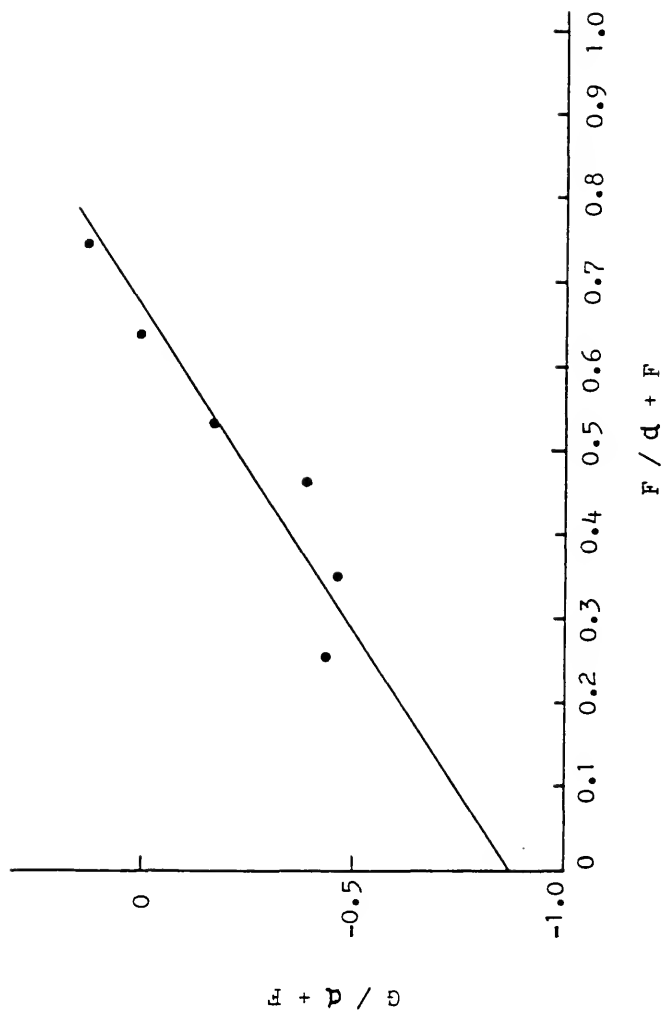


Figure 22. Plot According to the Method of Kelen-Tudos for the AN-DABD Copolymer System.

TABLE 23
Monomer Reactivity Ratios for the Free Radical
Initiated Copolymerization of DABD and AN

Calculation Method	$r_1(\text{DABD})$	$r_2(\text{AN})$
Fineman-Ross	0.49	0.52
Kelen-Tudos	0.44	0.49

As shown in Table 23, both r_1 (DABD) and r_2 (AN) are small, and hence suggest that there could be a highly alternating tendency for M_1 and M_2 in the AN-DABD copolymerization.

Microstructure of AN-DABD Copolymers

In the infrared spectra of AN-DABD copolymers, absorptions were seen at 730 cm^{-1} and 940 cm^{-1} which are characteristic of cis and trans-3,4 structures.

The ^1H NMR spectrum of AN-DABD copolymer is shown in Figure 23. Table 24 shows the assignments of chemical shifts in the ^1H NMR spectrum of AN-DABD copolymer.

The ^{13}C NMR spectrum of AN-DABD copolymer is shown in Figure 24. Along with off-resonance and INEPT spectra, the assignments of chemical shifts in Figure 24 are shown in Table 25.

The formation constant of DABD and AN system was determined by the ^1H NMR method using the equation that was developed by Foster and Fyfe.⁵⁴

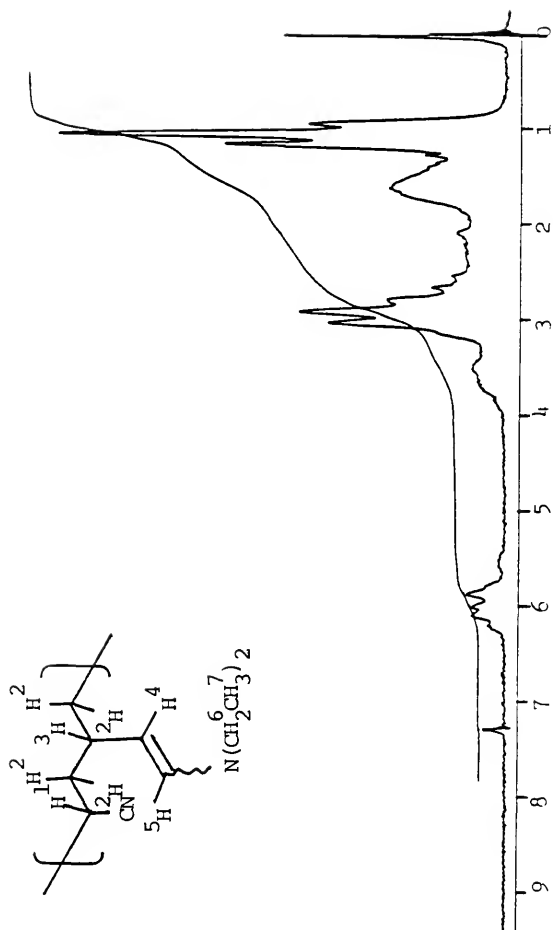


Figure 23. ^1H NMR (60 MHz) Spectrum of AN-DABD Copolymer in CDCl_3 at 25°C.

TABLE 24

Assignments of Chemical Shifts in ^1H NMR Spectrum
of AN-DABD Copolymer

Proton Assignments	Chemical Shifts δ (observed)	Chemical Shifts δ (calculated)	Number of Protons
5, 4	6.02, 3.50	5.71, 4.53	2
6, 1, 3	2.96		6
2	1.60	1.61	4
7	1.03		6

TABLE 25

Assignments of Chemical Shifts in ^{13}C NMR Spectrum
of AN-DABD Copolymer

Carbon Assignments	Chemical Shifts δ (observed)
2	139.68, 138.90
8	122.81, 121.94
1	94.98
6	44.45, 43.81
3	39.77, 38.40, 37.38
4, 5	27.34, 26.56
7	12.61

The proton chemical shifts of DABD were measured with various concentrations of AN in benzene- d_6 solution. Table 16 summarizes the results that were measured at 25°. By plotting $\Delta/[A]_0$ vs Δ , straight line was obtained, the slope and intercept permit the calculation of the formation constant. Based on the chemical shifts of methylene protons ($-NCH_2-$), the value of K_f calculated is 0.06 at 25°. Since the TMS was a poor reference substance for this system, the spectra were calibrated via a characteristic signal of the deuterated benzene. On the basis of these corrected chemical shift values, the value of K_f calculated is 0.15 at 25°.

The carbon chemical shifts of DABD were measured with various concentrations of AN in benzene- d_6 at 25°. The results are summarized in Table 17. The formation of 1:1 complex caused downfield shifts of methylene carbon ($-NCH_2-$) and olefinic carbons, C1 and C3. The DABD in the AN-DABD system may be related to the so-called " π -type" donor, i.e., π electrons of the donor partially transfer to the acceptor in the complex formation.

The relative reactivity of this comonomer pair in radical alternating copolymerization may be explained qualitatively in terms of frontier orbitals also. No trans-1,4 and cis-1,4 structures were formed; that may be attributed to the steric factor, i.e., the diethylamino group on the C1 position of DABD is bulkier than the ethoxy group on the C1 position of EBD.

Copolymerization of 1-Trimethylsilyloxy-1,3-butadiene and Acrylonitrile

The copolymerizations of 1-trimethylsilyloxy-1,3-butadiene (TSBD) with acrylonitrile (AN) were carried out by free radical or

spontaneous initiation in benzene at 60°. The reaction conditions and results are shown in Tables 5 and 6.

Microstructure of AN-TSBD Copolymers

In the infrared spectra of AN-TSBD copolymers, absorptions were seen at 970, 930 and 751 cm^{-1} , which are characteristic of trans-1,4, trans-3,4, and cis-1,4 structures, respectively.

The ^1H NMR spectrum of 1:1 molar ratio AN-TSBD copolymer is shown in Figure 25. On the basis of integration of the olefinic protons, the copolymers are composed of 41% trans-1,4 and cis-1,4 addition and 59% trans-3,4 addition. Table 26 shows the assignments of chemical shifts in the ^1H NMR spectrum of AN-TSBD copolymer, based on two polymer sequence units I and II.

The ^1H decoupled ^{13}C NMR spectrum of AN-TSBD copolymer is shown in Figure 26. Along with the off-resonance spectra, the assignments of the chemical shifts in Figure 26 are shown in Table 27, based on polymer sequence units I and II.

The AN-TSBD is similar to the AN-EBD system, so frontier orbital theory may also be used to explain qualitatively the relative reactivity of this comonomer pair in radical alternating copolymerization. Since the trimethylsilyloxy group is bulkier than the ethoxy group, the composition of trans-1,4 structure in the AN-TSBD copolymer is less than that in the AN-EBD copolymer.

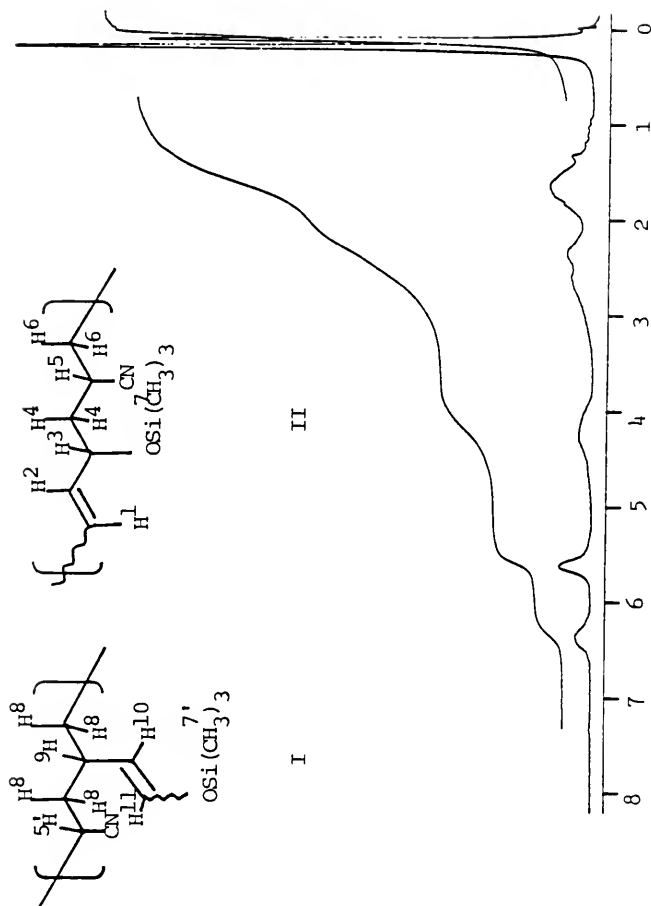


Figure 25. ^1H NMR (60 MHz) Spectrum of AN-TSBD Copolymer in CDCl_3 at 25°C .

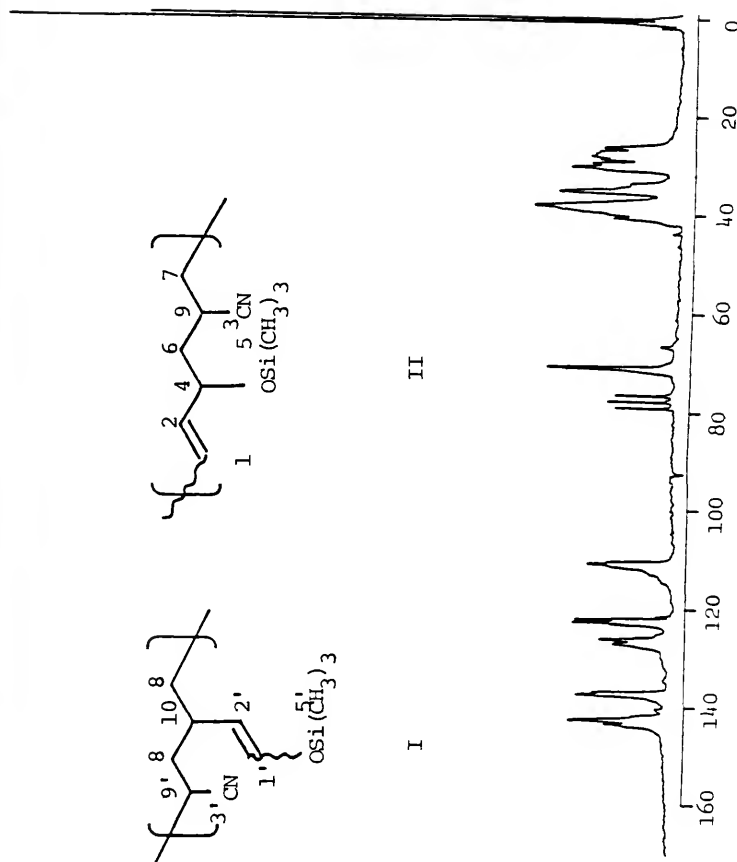


Figure 26. ¹H Decoupled ¹³C NMR (25.2 MHz) Spectrum of AN-TSBD Copolymer in CDCl₃ at 25°C.

TABLE 26

Assignments of Chemical Shifts in ^1H NMR Spectrum
of AN-TSBD Copolymer

Proton Assignments	Chemical Shifts δ (observed)	Chemical Shifts δ (calculated) ⁵²	Number of Protons
11	6.36	6.20	0.6
1, 2	5.60	5.46	0.8
3, 10	4.23	3.55, 4.66	1.0
5, 5'	2.60	2.60	1.0
6, 9	2.33	2.39	1.4
4, 8	1.67	1.61, 1.76	3.2
7, 7'	0.10, 0.18		9.0

TABLE 27
 Assignments of Chemical Shifts in ^{13}C NMR Spectrum
 of AN-TSBD Copolymer

Carbon Assignments	Chemical Shifts δ (observed)	Chemical Shifts δ (calculated) ⁵¹⁻⁵³
1'	142.50, 141.67	144
2	136.56	133.6
1	126.32, 125.30	130.6
3, 3'	122.28, 121.89, 121.25	
2'	110.09	106.5
4	70.42, 70.18	80.9
6	40.10, 37.62	36.1
7, 8	34.65	34.1, 33.0
9'	29.77, 28.90, 28.12	30.1
9, 10	26.07, 25.78	26.1, 24.0
5, 5'	0.10, -0.68	

Copolymerization of 1-Acetoxy-1,3-butadiene and Acrylonitrile

The copolymerizations of 1-acetoxy-1,3-butadiene (ATBD) with acrylonitrile (AN) were carried out by free radical or spontaneous initiation in benzene at 60°. The reaction conditions and results are shown in Tables 5 and 6.

Microstructure of AN-ATBD Copolymer

In the infrared spectra of AN-ATBD copolymers, absorptions were seen at 970, 936 and 754 cm^{-1} which are characteristic of trans-1,4, trans-3,4, and cis-1,4 structures, individually.

The ^1H NMR and ^{13}C NMR spectra of the resulting copolymer are shown in Figures 27 and 28, respectively. On the basis of integration of the olefinic protons, the copolymers are mainly composed of trans-1,4 addition. Along with the off-resonance spectra, the assignments of chemical shifts in Figure 28 are shown in Table 28, based on polymer sequence units I and II.

Copolymerization of 1-Ethoxy-1,3-butadiene and Ethyl α -Cyanoacrylate

The copolymerizations of 1-ethoxy-1,3-butadiene (EBD) with ethyl α -cyanoacrylate (ECA) were performed by free radical initiation in benzene at 60°. An appreciable amount of Diels-Alder adducts were formed as by-product. The reaction conditions and results are shown in Tables 9 and 10.

On the basis of the elemental analysis, the mole fraction of the acceptor was much higher than that of the donor in the copolymer. This result may suggest that the propagation step of the copolymerization was via the free monomer mechanism.

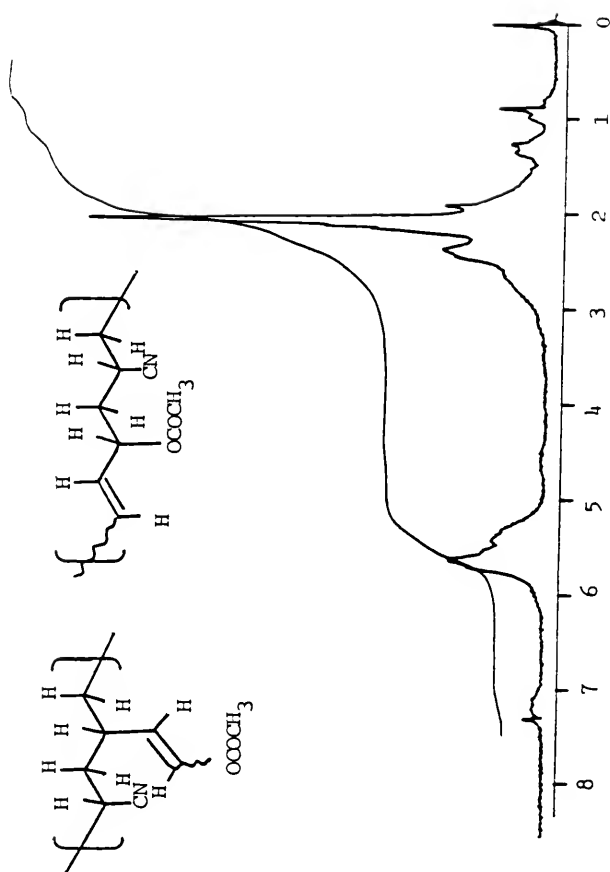


Figure 27. ^1H NMR (60 MHz) Spectrum of AN-ATBD Copolymer in CDCl_3 at 25°C .

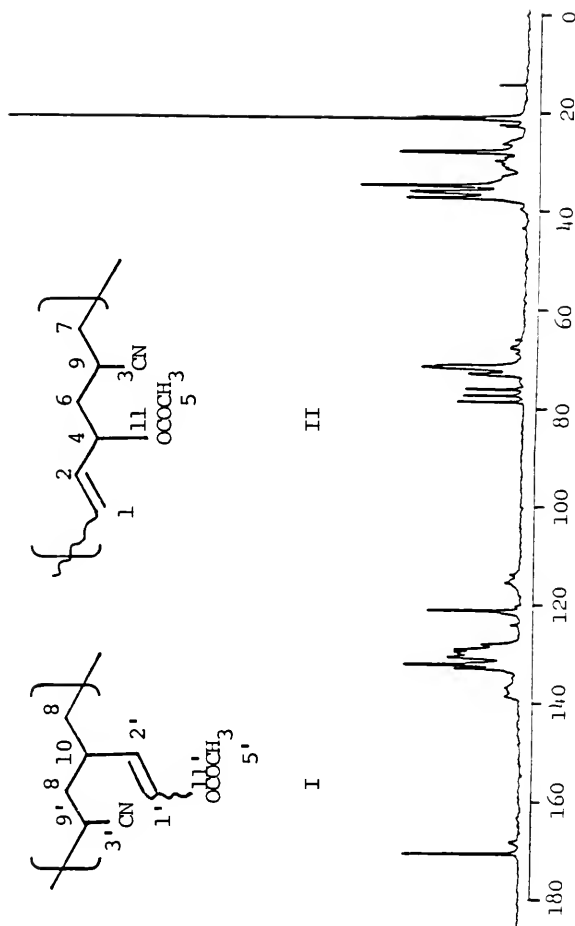


Figure 28. ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of AN-ATBD Copolymer in CDCl_3 at 25°C .

TABLE 28

Assignments of Chemical Shifts in ^{13}C NMR Spectrum
of AN-ATBD Copolymer

Carbon Assignments	Chemical Shifts δ (observed)	Chemical Shifts δ (calculated) ⁵¹⁻⁵³
11	169.80	
11'	167.60	
1'	137.97, 136.70	133.0
1, 2	132.32, 131.59, 130.08, 129.34 128.95, 128.56, 128.37, 127.39	131.6, 130.5
3, 3'	120.62	
2'	114.92	118.5
4	72.76, 72.56, 71.59, 71.35	74.9, 69.6
6	37.13	36.1
7, 8	35.82, 34.60	35.0, 33.0
9'	32.65, 31.14, 30.46, 29.58 28.85	30.0
9	27.78	27.1
10	26.07, 25.63	24.0
5, 5'	20.96, 20.47	

Copolymerization of 1-Ethoxy-1,3-butadiene and Fumaronitrile

The copolymerizations of 1-ethoxy-1,3-butadiene (EBD) with fumaronitrile (FN) were carried out by free radical initiation in benzene at 60°. The reaction conditions and results are shown in Tables 9 and 10.

The resulting copolymer was insoluble in most organic solvents. Judging from the elemental analysis, this copolymerization has a highly alternating tendency. Fumaronitrile did not homopolymerize due to the α -steric effect. This steric factor does not exist in ethyl α -cyanoacrylate. This may be the reason that the mole fraction of acceptor in the ECA-EBD system is much higher than that in the FN-EBD system.

Copolymerizations of Electron-Rich Dienes with Electron-Poor Dienes

Copolymerization of 1-Ethoxy-1,3-butadiene and Methyl 2,4-pentadienoate

The copolymerization of 1-ethoxy-1,3-butadiene (EBD) with methyl 2,4-pentadienoate (MPD) were carried out by free radical or spontaneous initiation in benzene at 60°. The reaction conditions and results are shown in Tables 7 and 8.

Microstructure of MPD-EBD Copolymers

In the infrared spectra of MPD-EBD copolymers, absorptions were seen at 965, 930, and 742 cm^{-1} which are characteristic of trans-1,4, trans-3,4, and cis-3,4 structures, respectively.

The ^1H NMR and ^{13}C NMR spectra of MPD-EBD copolymers are shown in Figures 29 and 30, individually. In Figure 30, the methine carbon

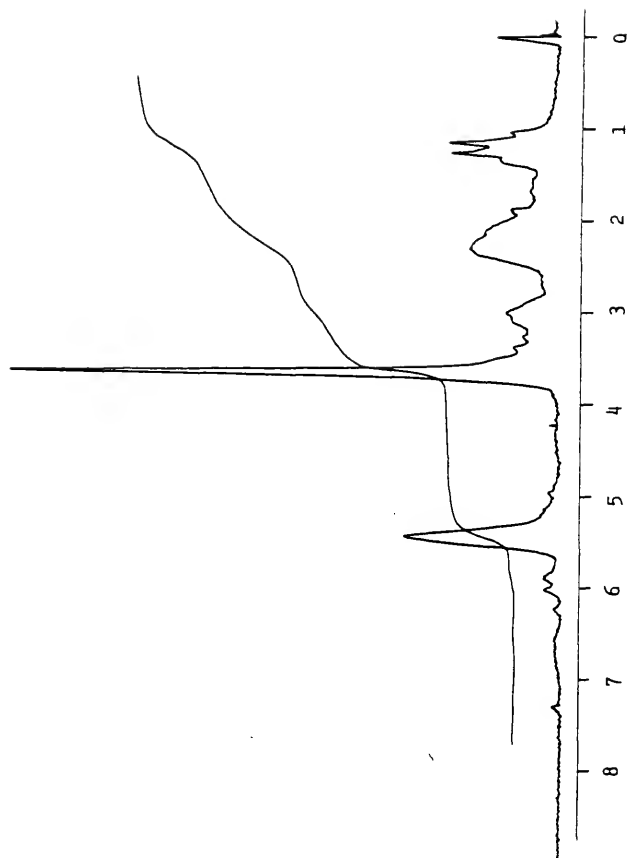


Figure 29. ^1H NMR (60 MHz) Spectrum of MPD-EBU Copolymer in CDCl_3 at 25°C .

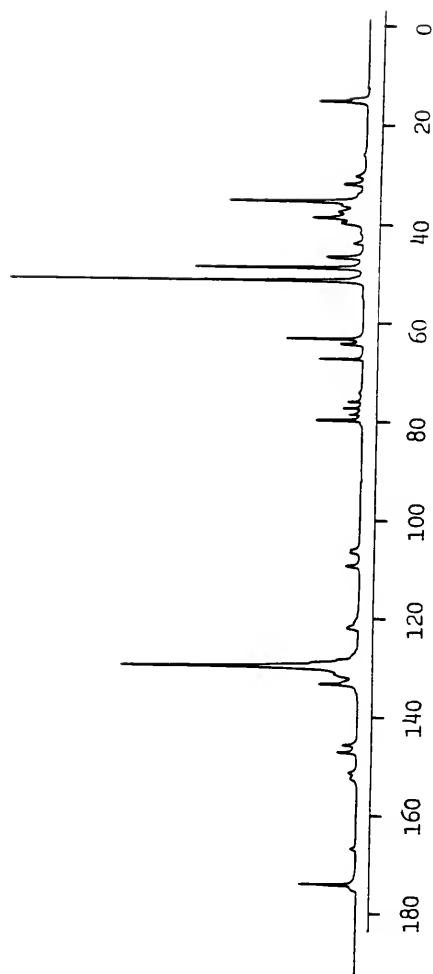
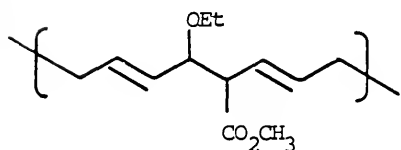
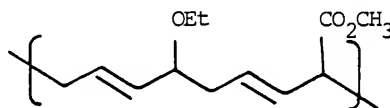


Figure 30. ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of MPD-EBD Copolymer in CDCl_3 at 25°C .

peak of the trans-1,4 structure of EBD monomer appeared at δ 79.5. Based on the ^{13}C NMR spectra of poly(MPD), the chemical shifts calculated for this carbon, the value is 86.2 for the structure I (head-to-head), and that is 82.8 for the structure II (head-to-tail).



Structure I



Structure II

Also, judging from the elemental analysis, the mole fraction of the acceptor was much higher than that of the donor in the copolymer. Both results may suggest that the copolymerizations of MPD and EBD proceed mainly via the free monomer mechanism under the polymerization condition used.

It was found that this comonomer pair could be copolymerized spontaneously. The donor-acceptor interaction between them may form a reactive intermediate to initiate the copolymerization.

Copolymerization of 1-Acetoxy-1,3-butadiene and Methyl 2,4-Pentadienoate

The copolymerizations of 1-acetoxy-1,3-butadiene (ATBD) with methyl 2,4-pentadienoate (MPD) were carried out by free radical initiation in benzene at 60°. The reaction conditions and results are shown in Tables 7 and 8.

In the infrared spectra of the MPD-ATBD copolymers, absorptions were observed at 970, 915, and 731 cm^{-1} which are characteristic of trans-1,4, trans-3,4, and cis-3,4 structures, respectively.

The ^1H NMR and ^{13}C NMR spectra of MPD-ATBD are shown in Figures 31 and 32, individually. Based on integration of the ^1H NMR spectrum, the MPD-ATBD copolymers were composed of 30% ATBD monomer units and 70% MPD monomer units.

Mechanism of Copolymerizations of Electron-Poor Dienes and Electron-Rich Dienes

The other copolymer systems, such as CBD (1-cyano-1,3-butadiene)-EBD, CBD-ATBD, and CCB (1-carbethoxy-1-cyano-1,3-butadiene)-ATBD, mole fractions of the acceptors were much higher than those of the donors in these copolymer systems. These observations suggest that the propagation steps of these copolymerizations proceed via the free monomer mechanism under the conditions used.

The frontier orbital theory may be used to explain this phenomenon. The frontier orbital energies and coefficients for 1-substituted diene acceptors and 1-substituted diene donors are shown in Figures 12 and 20, respectively.

For the polymerization system of electron-poor dienes and electron-rich dienes, the difference of HOMO energies between them is only 1.0 eV. So the SOMO-LUMO interaction may not be the only factor in these reactions. On the other hand, the difference of LUMO energies between them is 3.0 eV, and SOMO-LUMO interaction is always stabilizing. Therefore, the interaction of SOMO-LUMO should also be considered.



Figure 31. ^1H NMR (60 MHz) Spectrum of MPD-ATBD Copolymer in CDCl_3 at 25°C .

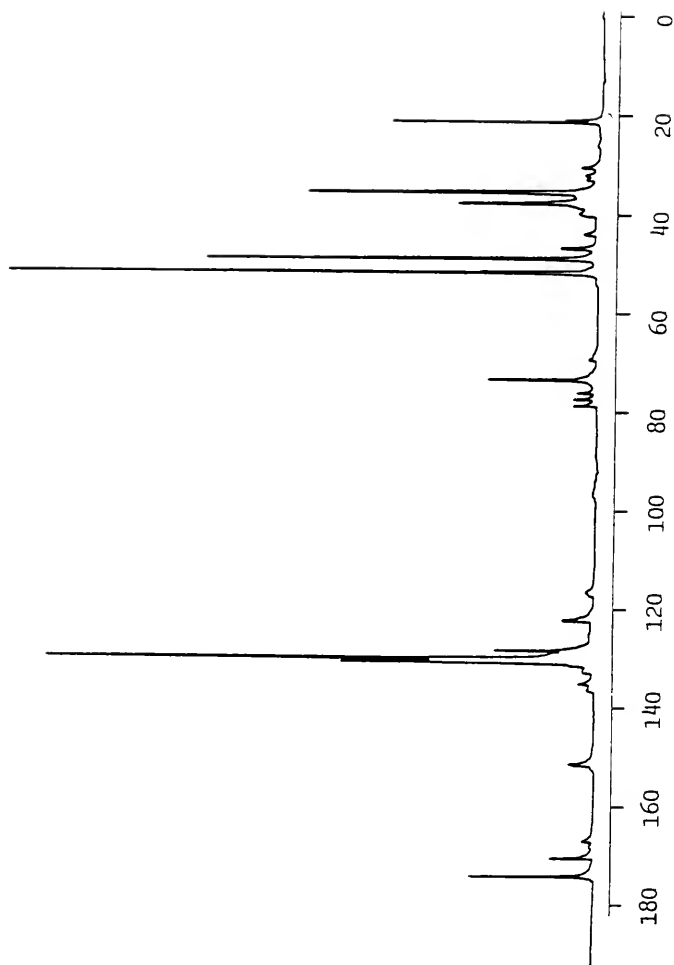


Figure 32. ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of MPD-ATBD Copolymer in CDCl_3 at 25°C .

Not only the energies of the frontier orbitals but also the coefficients of the corresponding atomic orbital are of importance in the interaction. In Figure 20, for 1-substituted electron-rich diene, the substituted LUMO coefficient is larger than the unsubstituted LUMO coefficient. On considering the orbital overlap factor, a free radical will attack the substituted position of this type of monomer. However, another factor, the steric α -effect will destabilize this interaction. For 1-substituted electron-poor dienes, the substituted LUMO coefficient is less than the unsubstituted LUMO coefficient (shown in Figure 12). A free radical would prefer to attack the unsubstituted position which does not involve the steric α -effect. Judging from these factors, we can successfully explain why resulting polymers were composed of more diene acceptor units.

Copolymerizations in Aqueous Phase

Copolymerizations of Trimethyl Vinyl Ammonium Bromide and Potassium Acrylate

The copolymerizations of trimethyl vinyl ammonium bromide (TVAB) with potassium acrylate (PA) were carried out in aqueous phase with azobis(2-amidinopropane)hydrochloride (V-50) as initiator. The reaction conditions and results are summarized in Table 11.

The ^1H NMR and ^{13}C NMR spectra of the resulting polymers are shown in Figures 33 and 34, respectively. The methyl protons of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) were used as an internal reference.

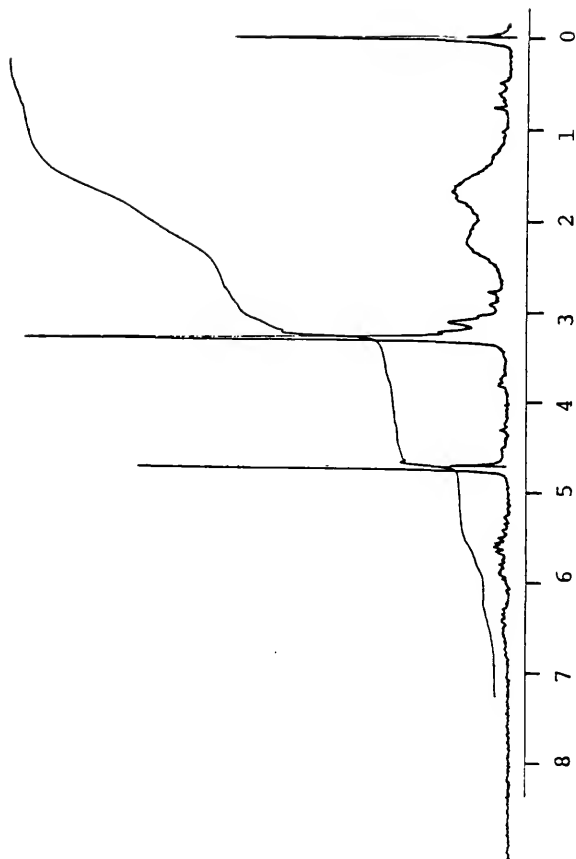


Figure 33. ^1H NMR (60 MHz) Spectrum of Poly(Trimethyl Vinyl Ammonium Acrylate) in D_2O at 25°C .

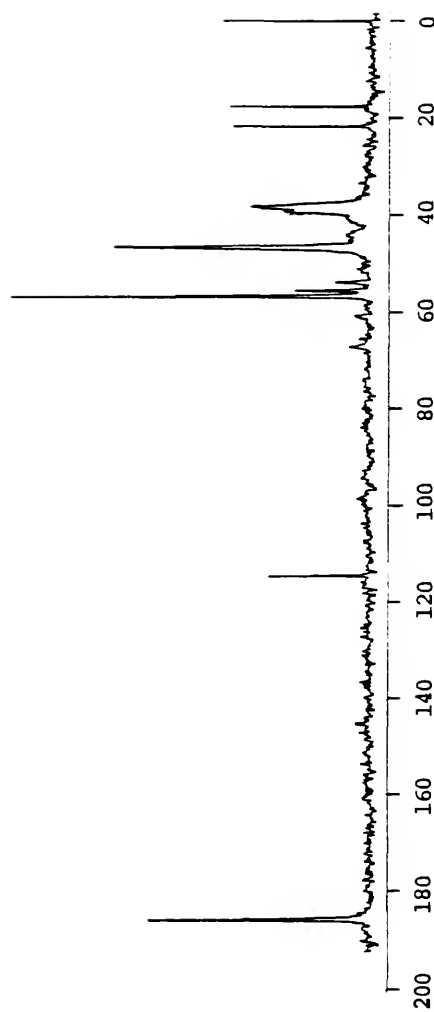


Figure 34. ^1H Decoupled ^{13}C NMR (25.2 MHz) Spectrum of Poly(Trimethyl Vinyl Ammonium Acrylate) in D_2O at 25°C .

On the basis of NMR spectra, the polymers were composed of polyacrylate as the polymer backbone, with trimethyl vinyl ammonium and potassium cations as counter ions.

Copolymerizations of Trimethyl Vinyl Ammonium Bromide and Potassium 2,4-Pentadienoate

The copolymerization of trimethyl vinyl ammonium bromide (TVAB) with potassium 2,4-pentadienoate (PPD) were carried out in aqueous phase with V-50 as initiator. The reaction conditions and results are summarized in Table 11.

On the basis of NMR spectra, the polymers are composed of trans-1,4 addition and trans-3,4 addition of poly(2,4-pentadienoate) as the backbone, with trimethyl vinyl ammonium and potassium cations as counter ions.

The intrinsic viscosity was measured with an Ubbelohde viscometer in 1 M sodium nitrate aqueous solution at 25°. The value was 0.71 dl/g.

Summary and Conclusions

In the investigation of copolymerization systems of diene acceptors (MPD, CCB, and CBD) and dienophile donors (BVE, CEVE, DOE, EVE, KEA, and KMA), it was shown that the resulting polymers were composed of diene monomer units only. These results indicate that the propagation steps of these polymerizations proceed via the free monomer mechanism under the conditions studied.

In the copolymerizations of diene donors (EBD, DABD, TSBD, and ATBD) and acrylonitrile (AN), the resulting copolymers were found to have equimolar composition by elemental analysis.

The formation constants of AN-EBD system and AN-DABD system were determined by the NMR method. The values of these constants were so small that the association between the comonomers may be weak.

The monomer reactivity ratios of the AN-EBD system and AN-DABD system were determined by the Fineman-Ross method and Kelen-Tudos method. Judging from the fact that the products of the monomer reactivity ratios are close to zero, these systems should have a high degree of alternation of monomer units in the equimolar copolymers.

On the basis of ^1H NMR and ^{13}C NMR spectra, these copolymers were shown to have highly alternating composition. Also, as judged from the chemical shifts calculated, the copolymers were mainly composed of head-to-tail sequence units. These observations suggest that the propagation steps of these systems proceed via the free monomer mechanism under the conditions studied.

These experimental results, such as the prevalence of head-to-tail configuration and the alternation tendency in the copolymers can be successfully explained by the frontier orbital theory.

In the copolymerizations of diene donors (EBD and ATBD) and diene acceptors (MPD, CCB, and CBD), it was shown that the mole fractions of acceptors were higher than those of the donors in the resulting copolymers. These results suggest that the propagation steps of these copolymerizations were via the free monomer mechanism under the conditions used.

REFERENCES

1. H.A. Benesi and J.H. Hildebrand, J. Am. Chem. Soc., 71, 2703 (1949).
2. R.S. Mulliken, J. Phys. Chem., 56, 801 (1952).
3. R.S. Mulliken and W.B. Person, "Molecular Complexes; A Lecture and Reprint Volume," Wiley-Interscience, New York, 1969.
4. M.J.S. Dewar, J. Am. Chem. Soc., 74, 3357 (1952).
5. K. Fukui, T. Yonezawa and H. Shingu, J. Chem. Phys., 20, 722 (1952).
6. E.M. Kosower, in "Progress in Physical Organic Chemistry," Vol. 3, S.G. Cohen, A. Stretwieser and R.W. Taft, Ed., Wiley-Interscience, New York, 1965.
7. F.R. Mayo and F.M. Lewis, J. Am. Chem. Soc., 66, 1594 (1944).
8. E. Merz, T. Alfrey and G. Goldfinger, J. Polym. Sci., 1, 75 (1946).
9. P.D. Bartlett and K. Nozaki, J. Am. Chem. Soc., 68, 1495 (1946).
10. J.A. Seiner and M. Litt, Macromolecules, 4, 308 (1971).
11. G.B. Butler, K.G. Olson and C.L. Tu, Macromolecules, 17, 1884 (1984).
12. G.B. Butler and K.C. Joyce, J. Polym. Sci., Part C (22), 45 (1968).
13. G.B. Butler and A.F. Campus, J. Polym. Sci., Part A-1, 8, 545 (1970).
14. G.B. Butler and Y.A. Ragab, J. Polym. Sci., Polym. Lett. Ed., 14, 273 (1976).
15. G.B. Butler and Y.A. Ragab, J. Polym. Sci., Polym. Chem. Ed., 19, 1175 (1981).
16. C. Caze and C. Loucheux, J. Macromol. Sci., Chem. A9, 29 (1975).

17. E.J. Goethals, A. Cardon and R. Grosjean, *J. Macromol. Sci., Chem.* A7, 1265 (1973).
18. S. Iwatsuki and Y. Yamashita, *Makromol. Chem.*, 89, 205 (1965).
19. T. Kokubo, S. Iwatsuki and Y. Yamashita, *Makromol. Chem.*, 123, 256 (1969).
20. N.G. Gaylord, M. Stolka, A. Takahashi and S. Maiti, *J. Macromol. Sci., Chem.* A5, 867 (1971).
21. N.G. Gaylord, M. Stolka and B.K. Patnaik, *J. Macromol. Sci., Chem.* A6, 1435 (1972).
22. C. Walling, E. Briggs, K. Wolfstirn and F.R. Mayo, *J. Am. Chem. Soc.*, 70, 1537 (1948).
23. T. Alfrey and C.C. Price, *J. Polym. Sci.*, 2, 101 (1947).
24. Y. Shirota, M. Yoshimura, A. Matsumoto and H. Mikawa, *Macromolecules*, 7, 4 (1974).
25. E. Tsuchida and T. Tomono, *Makromol. Chem.*, 141, 265 (1971).
26. J. Sauer, *Angew. Chem. Int. Ed. Engl.*, 6, 16 (1967).
27. I. Fleming, "Frontier Orbital and Organic Chemical Reaction," Wiley, London, 1976.
28. N.G. Gaylord, O. Solomon, M. Stolka and B.K. Patnaik, *J. Macromol. Sci., Chem.* A8, 981 (1974).
29. A.J. Gordon and R.A. Ford, "The Chemist's Companion: A Handbook of Practical Data, Techniques and References," John Wiley & Sons, New York, 1972.
30. S.M. McElvain and D. Kundiger, *Org. Synthesis*, 23, 45 (1943).
31. S.M. McElvain and H.F. McShane, Jr., *J. Am. Chem. Soc.*, 74, 2662 (1952).
32. M.B. Rubin, *Synthesis*, 266 (1977).
33. S. Hünig and H. Kahanek, *Chem. Ber.*, 90, 238 (1957).
34. W. Flaig, Reichsamt Wirtschaftsausbau, *Chem. Ber.*, 093(PB52020), 1073 (1942); *Chem. Abstr.*, 41, 6189g (1947).
35. J. Fueno, T. Tsunetsugu, K. Arimoto and J. Furukawa, *J. Polym. Sci., Part A-1*, 9, 163 (1971).

36. Y. Bando, T. Dodou and Y. Minoura, J. Polym. Sci., Polym. Chem. Ed., 15, 1917 (1977).
37. E.P. Kohler and F.R. Butler, J. Am. Chem. Soc., 48, 1036 (1926).
38. R. Worley and R.N. Young, Europ. Polym. J., 8, 1355 (1972).
39. A.I. Vogel, "Textbook of Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co., New York, 1956.
40. H.R. Snyder, J.M. Stewart and R.L. Myers, J. Am. Chem. Soc., 71, 1055 (1949).
41. A.H. Gerber, Polym. Prep., 9(1), 434 (1968).
42. D.E. Welton, U.S. Pat. 3,113,969, Dec. 10, 1963.
43. J.W. Cooper, in "Topics in Carbon-13 NMR," Vol. 2, G.C. Levy, Ed., John Wiley and Sons, New York, 1976.
44. D.P. Burum and R.R. Ernst, J. Mag. Res., 39, 163 (1980).
45. D.M. Doddrell and D.T. Pegg, J. Am. Chem. Soc., 102, 6388 (1980).
46. K.N. Houk, J. Am. Chem. Soc., 95, 4092 (1973).
47. F. Bernardi, N.D. Epiotis, W. Cherry, H.B. Schlegel, M.H. Whangbo and S. Wolfe, J. Am. Chem. Soc., 98, 469 (1976).
48. P.W. Tidwell and G.A. Mortimer, J. Polym. Sci., A3, 369 (1965).
49. M. Fineman and S.D. Ross, J. Polym. Sci., 5, 259 (1950).
50. T. Kelan and F. Tudos, J. Macromol. Sci., Chem. A9, 1 (1975).
51. F.W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra," Heyden and Son, Inc., Philadelphia, 1976.
52. R.M. Silverstein, G.C. Bassler and T.C. Morrill, "Spectrometric Identification of Organic Compounds," 4th Ed., John Wiley and Sons, New York, 1981.
53. G. Gatti and A. Carbonaro, Makromol. Chem., 175, 1627 (1974).
54. R. Foster and C.A. Fyfe, Trans. Faraday Soc., 61, 1626 (1965).

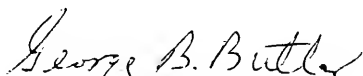
BIOGRAPHICAL SKETCH

Jen-Chi Chen was born on February 3, 1954, in Taipei, Taiwan, Republic of China. He received his B.S. degree in chemistry from the National Tsing-Hua University, Hsinchu, Taiwan, in 1976. After two years' military service, he spent one year at the National Taiwan University as a graduate student. In 1979, Mr. Chen joined the Department of Chemistry of the National Tsing-Hua University as a full-time teaching assistant. In 1980, he enrolled in the Graduate School of the University of Florida.

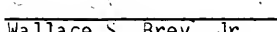
While working toward the degree of Doctor of Philosophy in organic chemistry, he served as a teaching and research assistant in the Department of Chemistry. He has presented one research paper at the ACS meeting in Raleigh, North Carolina, in 1984.

Mr. Chen was married to the former Weng-Jang Wang in August, 1979. He is the father of one lovely girl, Ida. The author is a member of the American Chemical Society.

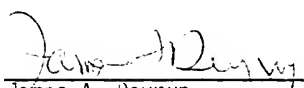
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


George B. Butler, Chairman
Professor of Chemistry

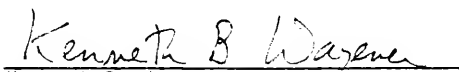
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Wallace S. Brey, Jr.
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


James A. Deyrup
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Kenneth B. Wagener
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Christopher D. Batich
Associate Professor of Materials
Science and Engineering

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry of the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1985

Dean, Graduate School

UNIVERSITY OF FLORIDA



3 1262 08553 5333